COLLOIDAL SULPHUR.

By

ASHWIN M. TRIVEDI, M.Sc. (Bombay).

Thesis for the Degree of Doctor of Philosophy.

University of Edinburgh. May 1941.

C O N T E N T S.

	Page.
INTRODUCTION	1
EXPERIMENTAL:	
Preparation of Sols	13
Methods of Chemical Analysis:-	
Determination of Chloride ...	16
Determination of Sulphur ...	18
Determination of Polythionate ...	19
Distribution of Electrolytes in Membrane Equilibrium	27
Distribution of Electrolytes between Coagulum and Supernatant Liquid	32
Distribution of Non-Electrolytes between Coagulum and Supernatant Liquid	38
Distribution of Non-Electrolytes in Membrane Equilibrium	44
DISCUSSION	46
SUMMARY	102

I N T R O D U C T I O N.

One of the most interesting facts in the field of inorganic colloids is the pronounced variation in the properties of colloidal sulphur as influenced by the method of preparation.(1)(2)(3)(4)(5) Indeed, two very definite types of sol may be distinguished on this basis, namely, (a) the von Weimarn type, prepared by physical methods, e.g., by the addition of an alcoholic solution of rhombic sulphur to a much larger volume of water, and (b) the Odén type, prepared by chemical methods, e.g., by the interaction of concentrated sulphuric acid with a solution of sodium thiosulphate, or by the interaction of sulphurous acid with hydrogen sulphide.

In particular, the sols behave in strikingly different ways towards electrolytes, as is shown by the following:

(i) Very much higher concentrations of the alkali metal salts are required for coagulation in the case of Odén sols than in the case of von Weimarn sols.

(ii) The minimum concentrations of these salts

---

(1) Freundlich and Scholz, Kolloidchem. Beih., 16 (1922) 234, 267.
(2) Freundlich, "Kapillarchemie", II (1933) pp.386-390.
(3) Freundlich, "New Conceptions in Colloidal Chemistry" (1926) p. 88.
(4) Odén, Nova Acta Upsala, Series IV, 3 (1913) No. 4.
(5) Bassett and Durrant, J.C.S., 1931, 2919.

necessary for the coagulation of Odén sols show a marked influence of the nature of the salt kation, the sequence of coagulating powers being Cs > Rb > K > Na > Li. Only slight differences in the same sense are shown by von Weimarn sols.

(iii) While von Weimarn sols are more readily coagulated by mineral acids than by corresponding alkali metal salts, the reverse holds for Odén sols.

(iv) Ion antagonism does not occur with von Weimarn sols, but is very marked in the case of Odén sols.

(v) The coagula obtained by the action of certain electrolytes on Odén sols are repeptised when the coagulant is removed. The coagulation of von Weimarn sols is irreversible.

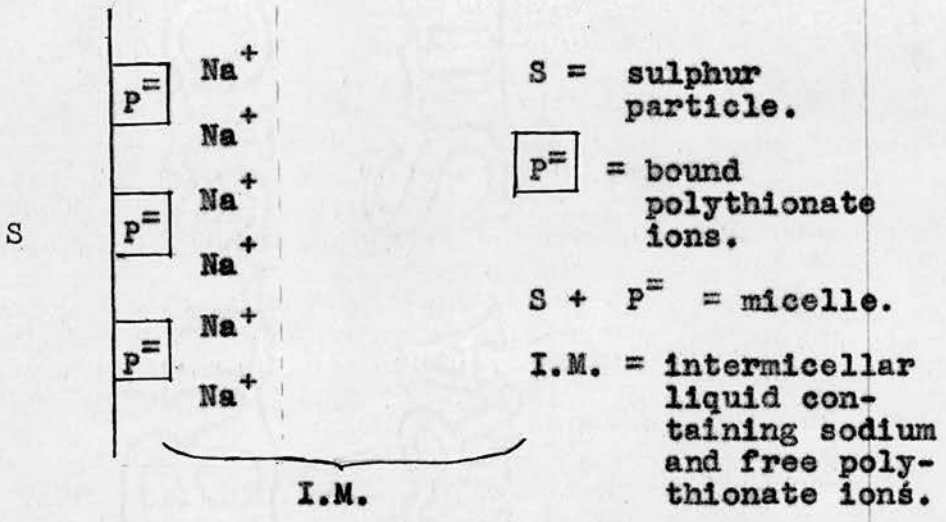
(vi) In the presence of certain electrolytes Odén sols may be coagulated by lowering the temperature, and the coagula repeptised by raising the temperature. Von Weimarn sols are not influenced by the temperature in this fashion.

As the result of the investigations of Freundlich and Scholz,[1] Bassett and Durrant,[2] and others,[3] it is certain that the special properties of the Odén type of sol are due to the presence in the colloidal micelles of polythionate, produced by chemical reactions involved in the formation of the sol. Bassett and

---

(1) Freundlich and Scholz, loc. cit.
(2) Bassett and Durrant, loc. cit.
(3) Bolam, Bowden, Muir and Currie, J.C.S., 1932, 2684; 1933, 1022; 1934, 754; 1939, 296.

Durrant have shown that when the sol has sufficiently aged, equilibrium is established between the polythionate "bound" by the sulphur, and the "free" polythionate dissolved in the intermicellar liquid.[1] Thus the following diagram gives an approximate picture of the constitution of the sol in the absence of foreign electrolytes:



The bound polythionate ions hold in their neighbourhood an equivalent amount of positive "counter-ions" (Gegenionen), which have a restricted range of movement, as indicated by the dotted line in the diagram.

On the addition of an electrolyte to the sol, interchange occurs between the added kations and the counter-ions of the sol. Bolam and co-workers[2] have investigated the interchange produced by the addition of salts to sols stabilised by polythionic acid and

---

(1) Bassett and Durrant have obtained evidence that the bound polythionate is probably hexathionate.
(2) Bolam etc., loc. cit.

thus containing hydrogen ions as counter-ions. In this case hydrogen ions are liberated from the immediate neighbourhood of the micelles, and appear in the intermicellar liquid to an extent depending upon the concentration and nature of the salt. Examination of the action of a considerable number of salts of various types indicated that the efficiency of a salt as a coagulant is closely related to the tendency of the salt kations to displace hydrogen ions from the neighbourhood of the micelles. To be precise, it was found that concentrations, of the various salts, which give the same degree of instability also produce the same degree of ionic interchange.

This result suggests that, in general, coagulation of Odén sols by electrolytes is due to neutralisation of the charge on the micelles by the adherence of kations of the coagulant to the polythionate ions bound by the micelles. On this view the order of the coagulating powers of a series of electrolytes will be the order in which they tend to adhere to the micelles.

It appeared possible to test the hypothesis of specific adherence of kations by employing the principle of the Donnan effect in the following way.(1) A sulphur sol, stabilised with sodium polythionate, and

---

(1) Compare Bjerrum, Z. physikal. Chem., 110 (1924) 656 ; Rinde, Phil. Mag., (S7) 1 (1926) 32 ; Ganguly and Krishnamurti, Trans. Faraday Soc., 24 (1928) 401 ; Ghosh, J.C.S., 1929, 2290, 2298 ; Ganguly, J. Phys. Chem., 31 (1927) 407.

containing sodium chloride in amount insufficient to cause coagulation, is placed on one side of a membrane, permeable to the simple electrolytes present, but impermeable to the colloidal sulphur. Water is placed on the other side of the membrane, so that when equilibrium is attained, we have, assuming the concentration of free polythionate to be negligibley small, essentially the conditions shown below.

m	Membrane	
	$P^{=}$	
	Cl^{-}	Cl^{-}
	Na^{+}	Na^{+}
	(1)	(2)

where $P^{=}$ = those bound polythionate ions to which sodium ions are not adhering.

According to Donnan's fundamental relation,

$$(a_{Na^+})_1 \ (a_{Cl^-})_1 = (a_{Na^+})_2 (a_{Cl^-})_2$$

where a = activity of respective ions. Hence

$$[Na^+]_1 = \frac{(f_{Na^+})_2 \ (f_{Cl^-})_2 \ [Na^+]_2 [Cl^-]_2}{(f_{Na^+})_1 \ (f_{Cl^-})_1 \ [Cl^-]_1}$$

where f = activity coefficient, and the square brackets denote equivalent concentrations.

Assuming

$$(f_{Na^+})_1 \, (f_{Cl^-})_1 = (f_{Na^+})_2 \, (f_{Cl^-})_2$$

we have $$[Na^+]_1 = \frac{[Na^+]_2[Cl^-]_2}{[Cl^-]_1} .$$

But $[Na^+]_2 = [Cl^-]_2$, and $[P^=] + [Cl^-]_1 = [Na^+]_1$.

Hence $$[P^=] = \frac{[Cl^-]_2^2 - [Cl^-]_1^2}{[Cl^-]_1} .$$

Thus the value of $[P^=]$ may be obtained by estimation of $[Cl^-]_1$ and $[Cl^-]_2$, where $[Cl^-]_1$ is the concentration of chloride in the intermicellar liquid of the sol. If the <u>total</u> concentration $[P^=]_a$ of the bound polythionate is also determined (by analysis), the proportion of non-adhering sodium counter-ions is given by the ratio $[P^=]/[P^=]_a$.

In the present research the procedure described above was applied to sols stabilised with sodium polythionate and containing sodium chloride, and to sols stabilised with polythionic acid and containing hydrochloric acid. These systems were selected because sodium chloride is a much more powerful coagulant than hydrochloric acid, and hence a large difference in the proportion of non-adhering counter-ions would be anticipated.

Since $[Cl^-]_1$, the amount of chloride in unit volume of the <u>intermicellar liquid</u>, has to be obtained

indirectly by measurement of the total chloride in unit volume of the sol, it is necessary to know (1)the volume occupied by the micelles, and (2) the amount of chloride, if any, adsorbed by the micelles.

Determinations of the volume occupied by the micelles are of value, not only for the purpose of deducing values of $[Cl^-]_1$, but also in connection with the important question of the "hydration" of the micelles. Freundlich attributes the characteristic behaviour of Odén sols to such hydration, and suggests that it is due partly to the attraction of water molecules by the oxygen atoms of the bound polythionate groups, and partly to the hydration of the counter-ions. For example, Freundlich and Scholz state, in their first paper,(1) that:

> "..... die ausgesprochen lyotrope Folge der Alkalimetallkationen, die bei den Odén'schen Solen auftritt, nicht bei den Weimarn'schen, ist mit der Hydratation der Mizellen zu verknüpfen. Die genannten Metalle geben wohl beständige Pentathionate. Es ist daher moglich, dass sich solche Pentathionate an dem Aufbau der Mixellen beteiligen, und dass ihre Anwesenheit deshalb eine bestimmte Hydratation der Mizellen bedingt. Dabei wird sich die Verwandtschaft dieser Kationen zum Wasser bemerkbar machen, die bekanntlich der lyotropen Reihe entspricht. Es wird also das Li - Ion, das die grösste Zahl Wassermolekule bindet, auch bevorzugt die Bestandigkeit erhöhen. Da die Adsorption dieser Ionen nur gering ist, demgemass auch die durch sie hervorgerufene Entladung, so kann ..... die durch die Hydratation veränderte Beständigkeit mit der durch die elektrische Ladung bedingten in Gegensatz treten. So erklären sich die auffallend grossen Flockungswerte dieser Kationen und die ausgepragte lyotrope Reihe."

(1) pp. 262 and 263.

Bassett and Durrant conclude from their observations that an Odén sol stabilised with sodium polythionate, for example, is essentially a solution of the sodium salt of a complex polythionic acid, and that the sol is "hydrophilic" simply because the ions of the complex salt are hydrated in the usual manner. Up to the present the existence of hydration has been deduced from qualitative observations of the behaviour and appearance of the sols and their coagula.(1) No attempt appears to have been made to obtain direct quantitative evidence of hydration, or to determine its amount under a variety of conditions.

In the present research the problem of hydration was approached by investigating the equilibrium distribution of raffinose between a sulphur sol (1) and an aqueous solution (2) separated by a membrane permeable to the sugar, but impermeable to the colloidal sulphur. Since the "reference substance" is a non-electrolyte, its concentration in the intermicellar liquid of (1) is the same as its concentration in (2). Also, the amount of raffinose in unit volume of the sol will differ from the amount in unit volume of the intermicellar liquid to an extent depending upon the volume occupied by the micelles, i.e., upon the volume occupied by the sulphur itself, and that of

---

(1) See Weiser and Cunningham, Colloid Symposium Monograph, VI (1928) 319 ; Dorfman, Koll. Z., 46 (1928) 186. 189. 52 (1930) 66 ; Dorfman and Ščerbačewa, Koll. Z., 52 (1930) 289.

any water, associated with the sulphur, which does not function as a solvent for the sugar. Hence measurements of the amounts of sugar in unit volumes of (1) and (2) suffice to determine the extent to which the micelles are hydrated, provided adsorption of raffinose by the sulphur is negligible, and provided also that a reasonable value can be assigned to the density of the sulphur.

The principle of the method has, of course, been frequently employed; for example, in the study of the hydration of simple ions,(1) of the micelles in soap solutions,(2) and of proteins.(3) Apparently, however, the method has not been previously used to obtain information about the hydration of the micelles in the case of any inorganic colloid.

It has already been pointed out that in order to obtain the values of $[P^{=}]/[P^{=}]_a$ by the procedure adopted in the present research, it is necessary to ascertain the extent to which chloride is adsorbed by the micelles. For this purpose, advantage was taken of the influence of temperature upon the stability of the sols. The amounts of sulphur and chloride in unit volume of a suitable sol were first determined. A portion of the sol was then coagulated by lowering the temperature, the sulphur allowed to settle, and the

---

(1) See, for example, Washburn, J.A.C.S., 31 (1909)322.
(2) McBain and Bowden, J.C.S., 123 (1923) 2417.
(3) Greenberg and Gunther, J. Biol. Chem., 85 (1929-30)491.
Greenberg and Greenberg, J. Biol. Chem., 94 (1931-32) 373.

amount of chloride in unit volume of the supernatant liquid estimated. But the difference between the chloride values depends not only upon the amount of chloride carried down by the coagulum, but also upon the volume occupied by the coagulum. This volume was determined by employing a reference substance as before, a known amount of sucrose or raffinose being added to a known volume of the sol, and the concentration of the sugar in the supernatant liquid determined after coagulation.

Determinations of the volume occupied by the coagulum are of value, apart from the question of the adsorption of chloride, since they yield information with regard to the hydration of the micelles after coagulation. As the following considerations show, such information is of fundamental importance.

It is usually assumed that the physical condition of the coagulum, and the tendency of the coagulum to repeptise, when excess of the coagulant is removed, depends upon the degree of hydration of the aggregated micelles. This has been tested in the present work by determinations of the volume occupied by coagula produced by the action of lithium, sodium, potassium, and barium salts.

Comparison of the degree of hydration of the micelles before and after coagulation shows to what extent dehydration has occurred and thus may provide an

essential clue to the nature of the coagulation process.

In conformity with their general standpoint, Bassett and Durrant remark that:[1]

> "Coagulation appears to be connected with, at least partial, neutralisation of the colloid particles. In the opinion of some, complete neutralisation is not necessary ..... , but our experiments appear to indicate that it is. For an electrolyte to be able to cause this neutralisation and coagulation, the ion of opposite sign to the micelle must be capable of forming with the micelle a salt (or, more generally, a product) which is insoluble in the surrounding liquid medium in the prevailing conditions. For this reason, those ions which normally form "insoluble" salts with the stabilising ion of the micelle are usually the most efficient coagulants for that particular sol. But the product formed by the coagulating ion and the micelle is probably always much more insoluble than the product formed by the union of the coagulating ion with the simple stabilising ion of the micelle, and for this reason many ions will coagulate a sol which would not, under similar conditions, give a precipitate with the stabilising ion alone .... Ions, such as sodium, which usually give soluble salts are not generally such efficient coagulants for negative sols as other positive ions such as potassium, barium, or thorium, which form less soluble salts ....."

Discussing the antagonistic action of certain kations, Bassett and Durrant further state that:[2]

> "..... with increase of concentration, something happens to the ions of an electrolyte which is variously ascribed to formation of unionised molecules or to decrease of activity. In this kind of way the polyvalent micelles of the sulphur sol, if in presence of hydrogen or sodium ions, become extensively occupied by these, so that coagulation of the sols by other ions forming less soluble products is largely prevented. The antagonistic action of the hydrogen, lithium, or sodium ions is due to the fact that micellar salts are formed which are largely acid, lithium, or

---

(1) pp. 2928, 2929.
(2) p. 2932.

> sodium salts and only partly salts of the other precipitating kation under test. They have the greater specific solubility characteristic of acids or of lithium or sodium salts, and so are much less readily precipitated. Hydrogen, lithium, or sodium ions, in sufficiently high concentration, can, however, themselves cause coagulation."

Judging from these statements, Bassett and Durrant appear to hold the view that mere neutralisation of the micelles (for example, by the formation of unionised molecules or ion-pairs) is not sufficient to cause coagulation. If the formation of <u>insoluble</u> complexes is an essential condition, it would seem to follow that dehydration of the micelles must also occur.

The foregoing indicates the main lines along which the present investigation was conducted. In the sequel a detailed account is given of the actual work, which involved several aspects additional to those already mentioned.

E X P E R I M E N T A L.

PREPARATION Of SOLS.

The three kinds of sol investigated were prepared as follows:-

Sodium Sol. A solution of 84 grams of sodium thiosulphate crystals in 50 ml. of water was slowly run into 65·5 ml. of concentrated sulphuric acid, the mixture being stirred mechanically. The temperature of the mixture was maintained at 25°C. (at which temperature the yield of colloidal sulphur is at its maximum, according to Odén)[1], the reaction vessel being surrounded by a freezing mixture of ice and salt. When addition was complete, 150 ml. of 4 molar sodium chloride were added, the coagulated sulphur filtered off by means of a Büchner funnel, and suction applied to remove all but a small part of the liquid. The coagulum was repeptised in 100 ml. of water by heating at 80°C., and the sol filtered to remove non-peptisable sulphur. Coagulation and peptisation were repeated until the sol obtained showed no trace of free acid when tested with litmus paper. As such a sol was

---

(1) Odén, Nova Acta (Upsala), Ser. 4, Vol. 3, No. 4 (1913) 50.

rather dilute, the whole of the above procedure was repeated several times, the final dispersion in each case being carried out in the sol from the first preparation. In the early stages of the work, the final concentrated sol was centrifuged for 15 minutes at 9000 revolutions per minute. Subsequently it was found that uncentrifuged sols became quite clear on being allowed to stand for some days. In the final stages of the work, the sols were, therefore, not centrifuged.

Sols prepared in the above manner are stabilised by sodium polythionate and contain sodium chloride as the only other electrolyte. They are therefore referred to as "sodium sols".

Hydrogen Sol. 100 ml. of sodium sol were coagulated with concentrated hydrochloric acid, the coagulum filtered off and peptised in 100 ml. of water. The coagulation and peptisation were repeated three to four times until the final dispersion showed the absence of sodium by the flame test. These sols are stabilised by polythionic acid and contain hydrochloric acid as the only other electrolyte. They are therefore referred to as "hydrogen sols".

Lithium Sol. To 100 ml. of sodium sol, 150 ml. of 8 N. lithium chloride were added. The coagulum was filtered off and repeptised in 100 ml. of water. This procedure was repeated four times and a sol, free

from sodium, obtained. These sols are stabilised by lithium polythionate and contain lithium chloride as the only other electrolyte present. They are therefore referred to as "lithium sols".

Fractionation of Sol. For one series of experiments, the lithium sol, prepared as above, was separated into two fractions in the following manner. To 200 ml. of sol, enough lithium chloride was added to make the sol 3 N. with respect to lithium chloride. The coagulum was filtered off and repeptised. This procedure was repeated thrice. The fraction of the sol which was completely coagulated by 3 N. lithium chloride is referred to as "lithium sol A." The filtrate from the first coagulum was then coagulated by the addition of a large excess of lithium chloride. The coagulum was filtered off and repeptised in 100 ml. of water. This sol is referred to as "lithium sol B".

Remarks. All the sols were stored in Jena glass bottles and kept in the dark.

All the chemicals used in the investigation, unless otherwise stated, were of A.R. or ANALAR quality.

Distilled water was employed throughout the work.

METHODS OF CHEMICAL ANALYSIS.

Determination of Chloride. Since a large number of chloride determinations had to be made during the course of the research, some time was spent in devising a suitable method for the rapid and accurate determination of chloride in the systems under investigation. The method ultimately selected was essentially that of Mohr, suitable modifications being introduced to meet the given conditions.

Since silver nitrate reacts with the polythionate, it was necessary to remove the polythionate before estimating chloride. Coagulation of the sol by the addition of salts would have left free polythionate behind[1] and was therefore not suitable from the point of view of chloride determination. Oxidation of the polythionate (to sulphate) by dilute nitric acid at 100°C. was found to be the most suitable method. When a portion of sulphur sol was boiled with nitric acid, the sulphur rapidly coagulated in the form of cakes. The perfectly clear supernatant liquid was free from polythionate, since silver sulphide was not formed on the addition of silver nitrate.

The actual procedure adopted for the determination of chloride was as follows. To a measured volume of sol, 25 ml. of 2 N. nitric acid were added

---

(1) Bassett and Durrant, J.C.S., (1931) 2924.

and the mixture diluted with distilled water so as to make the solution 0·5 N. with regard to the acid. The acidified solution was then gently boiled in a 250 ml. conical flask fitted with a rubber stopper, through which passed a small air condenser to prevent loss of hydrochloric acid by concentration of the solution. The concentration of the chloride was always less than 0·15 N. The time of decomposition varied from 10 to 30 minutes, but for the sake of uniformity all sols were heated for exactly half-an-hour. The warm solution was neutralised by the careful addition of calcium carbonate[1] (shown by experiment to be free from chloride), and filtered into a porcelain basin. It proved unnecessary to boil this solution, as the small amount of dissolved carbon dioxide had no influence on the end-point. 2 ml. of 2% potassium chromate solution per 100 ml. of the liquid were added and the solution titrated against standard silver nitrate solution in the manner described by Cumming and Kay.[2]

---

(1) A much sharper end-point was obtained with calcium carbonate than by neutralisation with sodium carbonate and subsequent acidification with acetic acid. This agrees with the recommendations of Mellor and Thompson ("A Treatise on Quantitative Inorganic Analysis", Second Edition (1938) 68) and Cumming and Kay ("A Text-book of Quantitative Chemical Analysis", 7th Edition (1939) 164).

(2) Cumming and Kay, loc. cit., 164, 165.

The silver nitrate solution was standardised against a standard sodium chloride solution of suitable concentration. The silver nitrate solution was kept in the dark and its normality checked from time to time.

The data in Table I show that the method was a reliable one for the present purpose, and in particular that no loss of chloride occurred as a result of the procedure adopted.(1)

TABLE I.

Solution titrated	Volume of 0·1 N. silver nitrate required (ml.).	
25 ml. of 0·1 N. sodium chloride	25·00 25·00	25·00
25 ml. of 0·1 N. sodium chloride treated as above	25·00 24·95	24·97

Determination of Sulphur. After boiling with nitric acid, the coagulated sulphur was collected in a Gooch crucible, heated in an oven at 120°C. until it melted, and then cooled and weighed. The heating was repeated until the weight of sulphur became constant. A small amount of sulphur was formed by the decomposition of the polythionate by the nitric acid. This amount, however, was negligible in comparison with the sulphur content of the sols.

---

(1) See also footnote on page 22.

Determination of Polythionate. In most cases polythionate was determined as silver sulphide, the procedure adopted being essentially the same as that followed by Bassett and Durrant.(1) For the determination of bound polythionate, 10 ml. of sol were coagulated with potassium chloride solution, the coagulum received on a filter paper and well washed with potassium chloride solution. The filter paper was pierced and the sulphur washed into a beaker with water, the temperature raised to 100°C., and silver nitrate acidified with nitric acid added. It was arranged that the silver nitrate was in slight excess and that the concentration of nitric acid in the final mixture was 0·2 N. The silver sulphide, sulphur and silver chloride were filtered off and the precipitate washed successively with water, cold dilute ammonia and hot water until the washings were free from chloride. The precipitate was then dried, the bulk of it removed from the filter paper, gently ignited in a crucible, cooled and weighed. The small amount of silver sulphide adhering to the paper was heated in a separate crucible and converted to metallic silver which was weighed and the corresponding weight of silver sulphide calculated and added to the weight of the main portion.

Treatment of the filtrate and washings from the separation of the coagulum (obtained by coagulating with potassium chloride), with silver nitrate and nitric acid

(1) Bassett and Durrant, loc. cit.

gave the amount of free polythionate present in the intermicellar liquid of the sol.

The decomposition of the polythionate may be expressed as

$$Ag_2S_xO_6 \longrightarrow Ag_2S + (x - 3)S + 2SO_3.$$

Thus, after the removal of silver sulphide, the polythionate may also be estimated by determination of the sulphate. In some instances both methods of analysis were employed, the procedure being as follows. The silver sulphide was filtered off and the excess of silver precipitated by the addition of dilute hydrochloric acid.(1) After removal of the silver chloride by filtration, the sulphate was precipitated by the addition of barium chloride and the barium sulphate collected and weighed in the usual manner.(2) It may be mentioned that it was found advantageous to wash the precipitate with cold water to diminish the tendency of the very fine precipitate to pass through the filter.

It will be seen from Table II (p. 21) that, in general, the agreement between the values obtained by the two methods was satisfactory. In this table, as elsewhere, the concentration of polythionate is expressed as milliequivalents per litre (m.e./l.) of sol.

---

(1) Cumming and Kay, loc. cit., 219.
(2) Cumming and Kay, loc. cit., 224.

TABLE II.

Reference	Weight (gm.) silver sulphide from 10 ml. sol	Weight (gm.) barium sulphate from 10 ml. sol	Polythionate (m.e./l.) By silver sulphide method (a)	Polythionate (m.e./l.) By barium sulphate method (b)	Ratio $\frac{a}{b}$
-	0·1319	0·2574	106·4	110·3	0·97
-	0·1379	0·2547	111·4	109·1	1·02
(c)	0·0384	0·0681	30·99	29·17	1·06
(d)	0·0184	0·0349	14·86	14·95	0·99
(e)	0·0051	0·0097	4·12	4·16	0·99
(f)	0·0066	0·0111	5·33	4·76	1·12
(g)	0·0130	0·0244	10·49	10·45	1·00
(h)	0·0162	0·0300	13·08	12·85	1·02
(i)	0·0205	0·0371	16·55	15·90	1·04
(j)	0·0220	0·0398	17·76	17·05	1·04
(k)	0·0206	0·0386	16·63	16·54	1·01
(l)	0·0222	0·0415	17·93	17·78	1·01
(m)	0·0051	0·0070	4·12	3·00	(1·37)
(n)	0·0058	0·0077	4·68	3·30	(1·42)
(o)	-	0·0225	-	9·64	-
(p)	-	0·0304	-	13·03	-

(c)	Table XVIII (b)	Experiment 10	Bound. Original Sol (O.S.). (1)
(d)	" "	"	Bound. Supernatant Liquid (S.L.). (2)
(e)	"	"	Free (O.S.). (1)
(f)	"	"	" (S.L.). (2)
(g)	"	Experiment 12	" (O.S.). (1)
(h)	"	"	" (S.L.). (2)
(i)	Table XIII (b)	Experiment 13	" (O.S.).
(j)	"	"	" (S.L.).
(k)	"	Experiment 14	" (O.S.).
(l)	"	"	" (S.L.).
(m)	Table XVIII (b)	Experiment 11	" (O.S.). (1)
(n)	"	"	" (S.L.). (2)
(o)	"	Experiment 13	" (O.S.). (1)
(p)	"	"	" (S.L.). (2)

A third method of determining polythionate was employed to check the reliability of the two methods described above. Both the sodium chloride and sodium polythionate in a sodium sol were converted into sodium sulphate by the action of sulphuric acid, and the sodium chloride determined as already described. Polythionate was then obtained as the difference between the total sodium and the sodium present as chloride.

The conversion to sulphate was carried out as follows. 25 ml. of sol were placed in a platinum basin and evaporated to dryness on a steam-bath. Sulphur was sublimed by heating with a very small flame, and 5 ml. of 5 N. sulphuric acid added to the residue, after cooling. The solution was very carefully evaporated to dryness and heated until all fumes of sulphuric acid had disappeared. The treatment with sulphuric acid was then repeated. Finally, a few lumps of ammonium carbonate (to remove traces of sulphuric acid) were added and the basin heated, at first gently and then strongly, until constant weight was obtained.

The results obtained are given in Table III (p.23) from which it will be seen that the sodium sulphate and the barium sulphate method agreed to within about 1 per cent.(1)

---

(1) This agreement provides further proof that the method used to determine the total chloride was reliable. It also follows that chloride is not adsorbed by the sulphur coagulum formed by treating a sol with hot nitric acid.

TABLE III.

	Expt. 1	Expt. 2	Expt. 3
Wt. sodium sulphate from 25 ml. sol (gm.)	0.3601	0·5344	0·4188
	0·3558	0·5349	0·4183
mean	0·3580	0·5347	0·4186
Vol. silver nitrate per 10 ml. sol (ml.)	10·40	18·75	12·95
	10·50	18·75	12·90
mean	10·45	18·75	12·93
Wt. barium sulphate per 10 ml. sol (gm.)	0·2298	0·2684	0·2551
	0·2291	0·2670	0·2531
mean	0·2295	0·2677	0·2541
Concn. Na (m.e./l.)	201·6	301·1	235·7
Concn. Cl (m.e./l.)	104·5	187·5	129·3
Polythionate (m.e./l.) from Na-Cl	97·0	113·6	106·4
Polythionate (m.e./l.) from barium sulphate	98·3	114·7	108·9
Ratio	0·99	0·99	0·98

From the foregoing, it is evident that the determination of polythionate as silver sulphide is quite satisfactory when the nitric acid is employed at a concentration of 0·2 N. Since Bassett and Durrant[1] state that the concentration of nitric acid may be varied between the limits 0·13 N. and 0·20 N., it might appear that the best results would be obtained with 0·16 N. acid. A number of analyses were carried out employing this concentration of the acid, but comparison with the results of parallel analyses by the sodium sulphate method showed definitely that the concentration of the acid was too low. As Table IV (p.25) shows, the values for polythionate by the silver sulphide method using 0·16 N. nitric acid, are on an average 50% higher than the values given by the sodium sulphate procedure.

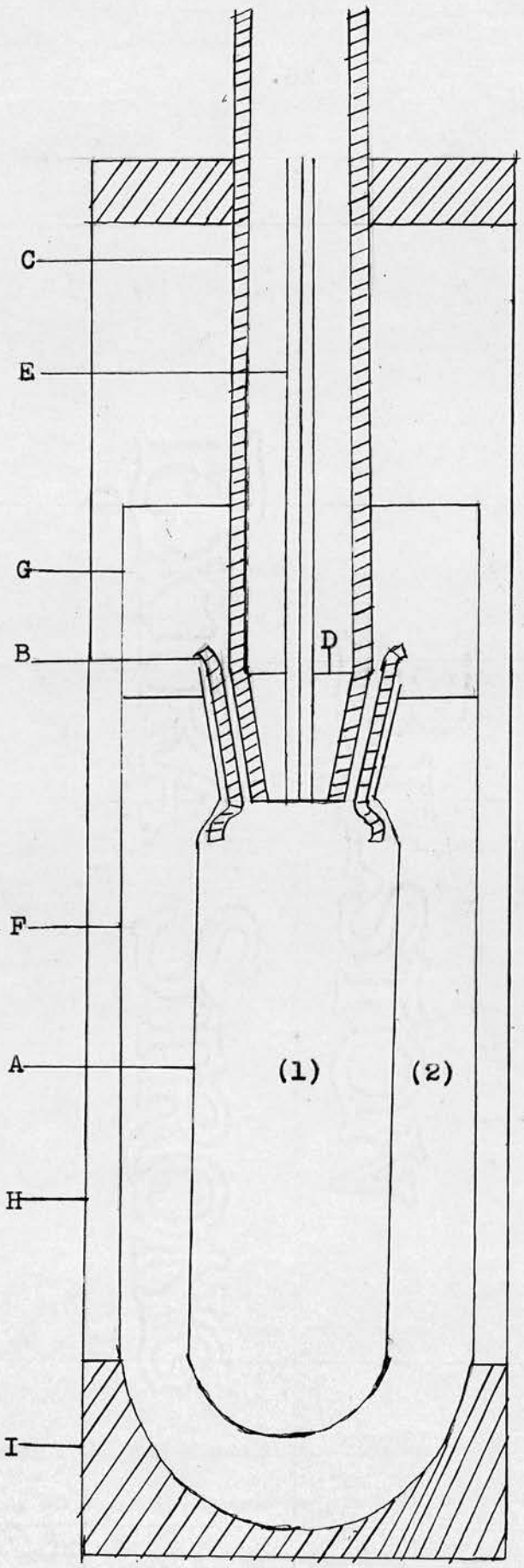
It should be added that Muir[2] obtained good agreement between values for bound polythionate determined by the sulphide method, using 0·20 N. nitric acid, and values obtained from measurements of the maximum ionic interchange.[3] Since Bassett and Durrant[4] also found this to be the case, it seems probable that they actually used 0·2 N. nitric acid, although regarding the above-mentioned limits as permissible.

---

(1) Bassett and Durrant, loc. cit., 2936.
(2) Muir, Thesis, Edinburgh (1934) 31.
(3) Bolam and Muir, J.C.S. (1933) 1026.
(4) Bassett and Durrant, loc. cit., 2936.

TABLE IV.

Expt.	Wt. sodium sulphate from 25 ml. sol (gm.)	Vol. 0·1 N. silver nitrate per 10 ml. sol (ml.)	Wt. silver sulphide from 10 ml. sol (gm.)	Conc. Na (m.e./l.)	Conc. Cl (m.e./l.)	Polythionate (m.e./l.)		Ratio
						from Na-Cl (a)	from silver sulphide (b)	b/a
1	0·4407	14·30 14·25 Mean 14·28	0·2089 0·2053 Mean 0·2071	248·2	142·8	105·4	167·2	1·59
2	0·2625	7·90 7·95 Mean 7·93	0·1407 0·1395 Mean 0·1401	147·8	79·3	68·5	113·1	1·65
3	0·3701	13·0 13·0 Mean 13·0	0·1542 0·1529 Mean 0·1536	208·4	130·0	78·4	124·0	1·58
4	0·6042	14·75 14·75 Mean 14·75	0·3594 0·3584 Mean 0·3589	340·2	147·5	192·7	289·7	1·50
5	0·4810	13·90 13·90 Mean 13·90	0·2407 0·2416 Mean 0·2412	270·8	139·0	131·8	194·7	1·48
6	0·3601 0·3558 Mean 0·3580	10.40 10·50 Mean 10·45	0·1806 0·1839 Mean 0·1823	201·6	104·5	97·01	147·2	1·52
7	0·5344 0·5349 Mean 0·5347	18·75 18·75 Mean 18·75	0·1959 0·1890 Mean 0·1925	301·1	187·5	113·6	155·3	1·37
8	0·4188 0·4183 Mean 0·4186	12·95 12·90 Mean 12·93	0·1763 0·1673 Mean 0·1719	235·7	129·3	106·4	138·8	1·31


C
E
G
B
D
F
A
(1)
(2)
H
I

DISTRIBUTION Of ELECTROLYTES In MEMBRANE EQUILIBRIUM.

In these experiments a study was made of the influence of colloidal sulphur upon the distribution of chloride in membrane equilibria. A diagram of the apparatus employed is shown in the figure on page 26. 50-60 ml. of sulphur sol (1) were placed in a collodion bag (A) securely fastened to the outer portion (B) of a ground-glass joint by means of a tight binding of thread. A piece of goldbeater's skin was wrapped round the collodion to avoid damage to the latter by the thread. The inner portion (C) of the glass joint was closed with a rubber stopper (D) through which passed a capillary glass tube (E). The bag was immersed in water (2) contained in a large glass tube (F), being held in position by a rubber stopper (G). In order to protect the sol from any action of the light, the apparatus was enclosed in a metal box (H). The apparatus was supported in a vertical position by the cork stand (I).

The collodion bags were prepared by coating the internal surface of a pyrex glass test-tube (2·5" × 19·5") with an absolute alcohol-ether (14 : 86) solution of collodion in the manner described by Hatschek(1).

---

(1) Hatschek, "Laboratory Manual of Elementary Colloid Chemistry" (1920) p. 22.

Although a 10% solution of collodion was employed[1] and the liquid allowed to drain slowly from the test-tube so as to give a thick-walled bag, it was not found possible to obtain a membrane which retained the whole of the colloidal sulphur.

Attempts to obtain an external solution free from sulphur by repeated changes of the water were unsuccessful and resulted in progressive decrease in the amount of colloidal sulphur within the membrane. Since, however, the concentration of sulphur inside the bag was, in general, much higher than that outside, the conditions were favourable for observation of the Donnan effect, if present, and in the later experiments the system was allowed to come to equilibrium without disturbance of any kind. In every case a period of a week was allowed, although evidence was obtained to show that equilibrium was reached in much less time than this. The osmotic pressure developed was very small and no attempt was made to measure it. Some formation of coarse sulphur occurred but the sols were quite clear when ready for sampling.

Most of the experiments were carried out at room temperature (16°-18°). In a few cases, the apparatus

---

(1) It is well-known that the higher the concentration of collodion, the less permeable is the membrane. In the present work it was found difficult to use solutions more concentrated than 10%.

was placed in an air-thermostat maintained at 25 $\pm$ 0·05°C. by means of electrical regulation. Another series of experiments were conducted at 0°C. in the following manner. The apparatus was placed in a metal box containing broken ice, the container in turn packed with wooden shavings in a wooden box which was kept in an ice-house. The ice in the container was renewed from day to day.

When equilibrium was attained, the sol (1) inside the bag, and the much weaker sol (2) outside, were analysed for chloride, sulphur, bound polythionate and free polythionate content. The actual experimental data are given in Tables V and VI (pp. 30 and 31).

TABLE V.

Estimation of Chloride and Sulphur.

Expt.	Normality of silver nitrate.	Volume (ml.) silver nitrate for 25 ml. liquid. (1)	(2)	Weight (gm.) sulphur from 10 ml. liquid. (1)	(2)
		Sodium Sols.			
1	0·0643	25·10	26·38	-	-
2	"	16·00	17·40	-	-
3	"	12·98	14·05	-	-
4	0·0635	10.10	11·02	0·4359	0·0639
5	"	18·75	19·15	0·1235	-
6	"	27·70	29·00	0·3028	0·0334
7	"	8·80	9·50	0·2337	0·0337
8	0·0625	5·70	5·85	0·0907	0·0114
9	"	11·30	12·00	0·2452	0·0408
10	0·04877	5·95(1)	6·45(1)	0·9201(1)	0·4262(1)
11	"	18·25	19·40	0·8831(2)	0·0941(2)
12	"	18·90(1)	21·50(1)	2·718(1)	0·6604(1)
13	"	17·65(1)	21·05(1)	3·589(1)	0·4214(1)
14	0·0500	18·75(1)	21·20(1)	2·829(1)	0·6456(1)
15	"	17·85(1)	19·43(1)	2·214(1)	0·7845(1)
16	"	11·35	11·88	1·187(2)	0·6041(2)
		Hydrogen Sols.			
17	0·05479	11·60	12·40	0·2786	0·0140
18	"	34·4 (3)	34·75(3)	0·2418	0·0258
19	"	10·00(3)	10·55(3)	0·2785	0·0020
20	0·04974	2·10	2·40	0 1316	0·0010
21	"	5·10	6·00	0·4200	0·0024
22	"	1·45	1·60	0·0790	0·0006
23	"	1·15	1·35	0·0892	0·0246
24	"	1·35	1·60	0·1770	0·0797
25	"	0·90	1·10	0·1728	0·0562
26	"	0·65	0·75	0·0640	0·0188
27	"	1·55	1·75	0·1386	0·0252
28	0·04938	1·55	2·00	0·2849	0·0550

(1) Value for 35 ml. liquid.
(2) Value for 25 ml. liquid.
(3) Value for 10 ml. liquid.
Experiments 10, 11, 12, 13 were carried out at 25°C., and
" 14, 15, 16 " " " " 0°C.

TABLE VI.

Estimation of Polythionate.

Expt.	Weight (gm.) silver sulphide			
	Bound Polythionate		Free Polythionate	
	(1)	(2)	(1)	(2)
Sodium sols				
1.	-	-	-	-
2.	-	-	-	-
3.	-	-	-	-
4.	0·0401	0·0070	-	-
5.	0·0205	0·0067	0·0043	0·0058
6.	0·0358	0·0051	0·0014	0·0011
7.	0·0227	0·0025	0·0008	0·0019
8.	0·0119	0·0047	0·0043	0·0035
9.	0·0271	0·0064	-	-
10.	0·0384	0·0184	0·0051	0·0066
11.	0·0474	0·0092	0·0051	0·0058
12.	0·1023	0·0256	0·0130	0·0162
13.	0·1010	0·0178	-	-
14.	0·0968	0·0282	-	-
15.	0·0819	0·0336	-	-
16.	0·0650	0·0382	-	-
Hydrogen sols				
17.	0·0186	0·0029	0·0010	0·0015
18.	0·0194	0·0041	0·0031	0·0029
19.	0·0264	0·0009	0·0022	0·0029
20.	0·0103	0·0012	0·0016	0·0016
21.	0·0305	0·0024	0·0019	0·0020
22.	0·0054	0·0012	0·0015	0·0016
23.	0·0105	0·0048	0·0014	0·0021
24.	0·0190	0·0105	0·0032	0·0035
25.	0·0170	0·0078	0·0028	0·0035
26.	0·0111	0·0040	0·0011	0·0020
27.	0·0130	0·0058	0·0014	0·0015
28.	0·0211	0·0094	0·0022	0·0024

DISTRIBUTION Of ELECTROLYTES Between COAGULUM And SUPERNATANT LIQUID.

Coagulation by Sodium Chloride. A portion of sodium sol containing sodium chloride of suitable concentration was placed in a tightly-stoppered Jena glass bottle and kept at 0°C. for four hours, when the bulk of the sulphur had coagulated. Most of the somewhat turbid supernatant liquid was decanted into another Jena glass bottle and usually allowed to attain room temperature. Portions of the liquid, which was now quite clear, were analysed for the content of sulphur, chloride and bound and free polythionate. Similar analyses were also made on a second portion of the original sol kept at room temperature.

The object of lowering the temperature was to produce coagulation by concentrations of sodium chloride which could be estimated with the necessary degree of accuracy. Coagulation by sodium chloride at room temperature requires a relatively high concentration of the salt.

The experimental data are given in Tables VII and VIII (pp. 33 and 34). In experiments 13 and 14, the supernatant liquid and a portion of the original sol were brought to 25 ± 0·05°C. (by enclosure in an air-thermostat) before the analyses were made.

TABLE VII.

Estimation of Chloride and Sulphur.

Expt.	Normality of silver nitrate solution	Vol. (ml.) silver nitrate for 10 ml. liquid		Wt. (gm.) sulphur from 10 ml. liquid	
		Original sol	Super-natant liquid	Original sol	Super-natant liquid
1	0·09805	32·6(1)	34 ·2(1)	2·1224(1)	0·5978(1)
2	"	29·9(1)	30·8(1)	1·6516(1)	0·5523(1)
3	"	47·8(1)	50·3(1)	0·7014	0·1570
4	"	9·95	10·35	0·9990	0·5834
5	"	20·45	22·25	1·1425	0·0675
6	"	13·65	14·10	0·7319	0·2718
7	0·1000	18·80	20·20	0·9637	0·1279
8	"	21·55	23·45	1·0326	0·0814
9	"	18·55	20·10	0·9957	0·0518
10	"	18·35	19·75	0·9635	0·1352
11	"	15·95	17·15	1·1384	0·1912
12	"	24·90	26·35	0·7078	0·0240
13	"	18·00	19·38	1·2336	0·4058
14	"	20·45	22·05	1·1956	0·3036

(1) Value for 25 ml. liquid.

TABLE VIII.

Estimation of Polythionate.

Expt.	Weight (gm.) silver sulphide from 10 ml. liquid.			
	Bound Polythionate		Free Polythionate	
	Original sol	Supernatant liquid	Original sol	Supernatant liquid
1	0·0798	0·0320	-	-
2	0·0598	0·0329	0·0120	0·0133
3	0·0927	0·0282	0·0346	0·0386
4	0·1115	0·0720	0·0283	0·0321
5	0·1277	0·0142	0·0300	0·0342
6	-	-	-	-
7	0·1163	0·0228	0·0190	0·0202
8	0·1307	0·0168	0·0163	0·0202
9	0·1316	0·0113	0·0210	0·0243
10	0·1222	0·0229	0·0156	0·0192
11	0·1369	0·0386	0·0488	0·0548
12	0·0823	0·0038	0·0237	0·0260
13	0·1535	0·0796	0·0205	0·0220
14	0·1504	0·0654	0·0206	0·0222

Coagulation by Nitric Acid. 35 ml. of 1·0 N. nitric acid were added to 25 ml. of sodium sol and the mixture heated in a tightly-stoppered Jena glass bottle at 80°C. until the sulphur was wholly coagulated (through decomposition of the polythionate as already described). 35 ml. of water were added to another 25 ml. of the sol and the mixture heated under the same conditions. After heating, both mixtures were brought to 25°C. in an air-thermostat. The supernatant liquid from the coagulated sol was analysed for chloride, and the uncoagulated sol for sulphur and chloride.

The experimental data are given in Table IX (p.37).

Coagulation with Potassium Nitrate. 25 ml. of sodium sol were completely coagulated by the addition of 25 ml. of 0·5 N. potassium nitrate. The sulphur was collected on a small ashless filter paper. The first portions of the filtrate were discarded and the concentration of chloride in the remainder of the filtrate determined, after decomposition of the free polythionate.

Another 25 ml. of sol were diluted with 25 ml. of water and the content of chloride and sulphur estimated in the usual way. Solid potassium nitrate was added to ensure that the conditions for the titration with silver nitrate were the same as in the

first part of the experiment.[1]

Experimental data are given in Table IX (p. 37).

Coagulation with Barium Nitrate. 25 ml. of sodium sol were completely coagulated by the addition of 25 ml. of 0·2 N. barium nitrate and the sulphur separated from the supernatant liquid by filtration. The first portions of the filtrate were discarded and the concentration of chloride in the remainder was determined after decomposition of the free polythionate. Sodium sulphate was added to precipitate the barium before commencing a titration.

25 ml. of the sol were diluted with 25 ml. of water and the concentration of sulphur and chloride determined. The conditions during the titration with silver nitrate were kept the same as in the first part of the experiment by the addition of suitable amounts of barium nitrate and sodium sulphate.

The experimental data are given in Table IX (p. 37).

---

(1) SeeCarpenter, Jour. Soc. Chem. Ind., 5 (1886) 286.

TABLE IX.

Expt.	Coagulant	Wt. (gm.) of sulphur from 10 ml. sol.	Volume (ml.) 0·1 N. silver nitrate for 10 ml. liquid.	
			Sol	Supernatant liquid
1	Nitric acid	36·28	15·83	16·13
2	"	100·22	21·13	22·28
3	"	64·26	39·75	41·15
4	Potassium nitrate	54·15	23·60	24·15
5	"	59·24	10·80	11·18
6	Barium nitrate	47·60	17·73	18·23
7	"	60·64	14·97	15·47

DISTRIBUTION Of NON-ELECTROLYTES. Between COAGULUM And SUPERNATANT LIQUID.

Experiments with Sucrose. These experiments were carried out with sodium sols and the chlorides of potassium, barium, lithium and sodium were employed as coagulants.

The procedure in the case of potassium or barium chloride will be clear from the following description of a typical experiment. Exactly 10 gm. of sucrose (ordinary) were placed in each of two 50 ml. flasks, and 30 ml. of sol then measured into one of the flasks and 30 ml. of water into the other. The sugar was dissolved by heating to about 40°C., the solutions cooled to room temperature and the same amount of solid potassium (or barium) chloride added to each. After the salt had completely dissolved, the volume in each case was made up to 50 ml. with water and the mixtures thoroughly shaken. The supernatant liquid from the completely coagulated sol was filtered free from suspended coarse sulphur and the rotation determined in the polarimeter. A portion of the solution (the "comparison solution") in the other flask was similarly treated. In addition, the concentration of the sulphur in the original sol was determined experimentally. Let this be x gm. per litre. Then the concentration[1]

(1) Values in column (a) in Table X.

of the sulphur in the final sol produced by dilution to 50 ml. (as described above) was 30x/50 gm. per litre.

The experimental data are shown in Table X (p.40).

With lithium chloride as coagulant, the procedure was the same as described above, except that the mixtures were cooled to 0°C. in order to increase the amount of coagulation. A sample of the (transparent) supernatant liquid from the coagulated sol and a sample of the comparison liquid were taken, allowed to reach room temperature and their rotations then measured. The concentrations of sulphur in the original sol and in the supernatant liquid were also determined. Although as will be seen from Table X, which gives the experimental data, the supernatant liquid contained colloidal sulphur, the concentration of this was always so low that a satisfactory determination of the rotation could be made.

Since the sol already contained sufficient sodium chloride, coagulation by this salt was effected by simply lowering the temperature of the sol to 0°C. Apart from this, the same procedure was employed as in the case of lithium chloride. In addition, the chloride content of the final sol and the supernatant liquid were estimated in two of the experiments.

The polarimeter was of the Schmidt and Hansch type and light of wave-length 5900 Å.U. (sodium D line) was employed for the measurement of the rotation. Two

TABLE X.

Sucrose.

Expt.	Weight (gm.) sulphur in one litre of: Final sol (a)	Supernatant liquid (b)	Difference (a)-(b)	Rotation (degrees) for Comparison solution (c)	Supernatant liquid (d)	Difference (d)-(c)
Coagulant: 0·2 N.(approx.) sodium chloride. Length of polarimeter tube = 1 dcm.						
1	60·87	37·64	23·23	13·28	13·51	0·23
2	102·72	6·60	96·12	13·28	14·16	0·88
3(1)	102·78	13·56	89·22	13·31	14·24	0·93
4(2)	102·34	21·20	81·14	13·28	14·17	0·89
Coagulant: lithium chloride.(3) Length of polarimeter tube = 1 dcm.						
5	85·07	22·76	62·31	12·68	13·48	0·80
6	86·20	23·56	62·64	12·79	13·51	0·72
7	86·20	22·76	63·44	12·79	13·59	0·80
8	81·86	10·46	71·40	12·79	13·67	0·88
Coagulant: 0·2 N.(approx.) potassium chloride. Length of polarimeter tube = 1 dcm.						
9	86·59	0·00	86·59	13·32	13·96	0·64
10	83·16	0·00	83·16	13·33	13·97	0·64
11	96·92	0·00	96·92	13·35	14·03	0·68
12	81·86	0·00	81·86	13·35	13·95	0·60
Coagulant: 0·1 N.(approx.) barium chloride. Length of polarimeter tube = 2 dcm.						
13	47·87	0·00	47·87	26·69	27·38	0·69
14	94·09	0·00	94·09	26·69	28·07	1·38

(1) Vol. (ml.) 0·1 N. silver nitrate for 5 ml. sol = 9·32.
" " " " supernatant liquid = 9·95.

(2) " " " " sol = 8·84.
" " " " supernatant liquid = 9·50.

(3) Concn. of coagulant was 4·8 N.(approx.) in expt. 5 and 3·9 N.(approx.) in expts. 6, 7 and 8.

polarimeter tubes, with fused ends and a central cup for filling, were used, the one being one decimetre and the other two decimetres in length. The tubes were always placed in the polarimeter so that the cup was quite horizontal. Before use, the tubes were thoroughly washed with water, rinsed with alcohol and ether, and dried with a stream of air. The measurements were made at room temperature (14°C. - 18°C.) which varied so slowly that it could be regarded as constant during the period required to complete the readings for any one experiment. The zero reading was found to be the same, whether the tube was empty or filled with distilled water. Individual readings of the rotation could be made to 0·01° . At the concentrations concerned, potassium, barium and sodium chlorides were found to have a negligible influence upon the rotation of the sucrose, whereas in the case of lithium chloride there was a considerable effect.[1] The difference between the concentration of the lithium chloride in the comparison solution and that in the supernatant liquid was, however, so very small that no correction is needed.

It was found that the addition of sucrose in sufficiently large amount produced coagulation of the sol. The concentration of the sugar was therefore

---

(1) cf. Washburn, J.A.C.S., 31 (1909) 339.

kept at 20% in order to avoid this complication.

Experiments with Raffinose. The lithium sols A and B (see p. 15) were employed in the experiments with raffinose as reference substance. Coagulation was brought about by adding lithium or sodium chloride and then cooling the sol to 0°C. The experiments were carried out exactly as described for sucrose with lithium chloride as coagulant. In every case 5 gm. raffinose ($C_{18}H_{32}O_{16}5H_2O$)(obtained from Hopkin and Williams) were present in 50 ml. of final sol or comparison liquid.

Under the given conditions, the sodium chloride was found to effect the rotations to a negligible extent, whereas the rotation was increased by the addition of lithium chloride.[1] As in the case of sucrose, no correction was needed for this effect of the lithium chloride, since comparison was made between liquids which differed only slightly in regard to the concentration of the salt.

The concentrations of sulphur and bound polythionate in sols A and B were determined.

The experimental data are given in Table XI (p. 43).

---

(1) Cf. Washburn, J.A.C.S., 31 (1909) 338.

TABLE XI.

Raffinose.

Expt.	Weight (gm.) sulphur in one litre of			Degrees rotation (2 dcm. tube) for		
	Final sol	Supernatant liquid	Difference	Comparison solution	Supernatant liquid	Difference.
	(a)	(b)	(a)-(b)	(c)	(d)	(d)-(c)
Lithium sol A. Coagulant: 3·2 N. lithium chloride.						
1	73·01	5·17	67·84	21·08	22·16	1·08
2	72·65	5·25	67·40	21·08	22·14	1·06
Lithium sol A. Coagulant: 1·0 N. sodium chloride.						
3	73·01	0·00	73·01	20·98	22·07	1·09
4	72·65	0·00	72·65	20·98	22·10	1·12
Lithium sol B. Coagulant: 1·0 N. sodium chloride.						
5	66·62	0·00	66·62	20·98	22·13	1·15
6	67·02	0·00	67·02	20·98	22·12	1·14

Weight of silver sulphide from bound polythionate in 5 ml. sol A = 0·0680 gm., and in 5 ml. sol B = 0·0737 gm.

DISTRIBUTION Of NON-ELECTROLYTES In MEMBRANE EQUILIBRIUM.

A quantity of sodium or lithium sol, containing raffinose, was placed in a collodion bag suspended in water in the manner previously described (pp. 27 - 29). The apparatus was kept in an air-thermostat at 25° ± 0·05°C. for a week. Equilibrium having been thus established, 10 ml. of sol (1) (inside bag) and of sol (2) (outside bag) were withdrawn and the content of sulphur determined. In addition, the sulphur in 35 ml. of each of the sols was completely coagulated by the addition of the same amount of solid barium chloride, and the rotation of the supernatant liquid (liquid (1) and (2) respectively) ascertained in the usual way.

The experimental data are given in Table XII (p. 45).

TABLE XII.

Raffinose.

Expt.	Weight (gm.) sulphur in one litre of		Differences in weight of sulphur	Degrees rotation (2 dcm. tube) for Supernatant liquid from	
	(1)	(2)	(1)-(2)	(1)	(2)
Sodium Sol					
1	82·40	14·86	67·54	31·01	31·91
2	122·12	3·73	118·39	28·43	30.74
3	80.80	16·07	64·73	42·08	43·58
Lithium Sol					
4	81·54	3·10	78·44	19·89	20·41
5	67·82	14·76	53·06	25·89	26·30

D I S C U S S I O N.

The data in Table V (p. 30) show how chloride is distributed between two Odén sols, of unequal sulphur concentrations, when the sols are separated by a membrane permeable to simple electrolytes, but impermeable to at least a portion of the colloidal sulphur. It will be seen that when equilibrium is established, the amount of silver nitrate equivalent to the total chloride in a given volume of the more concentrated sol (1) is in all cases less than that equivalent to the total chloride in the same volume of the less concentrated sol (2). In the majority of cases, the difference in titre is well outside the experimental error (about $\pm$0·10 ml. at the most). Moreover, the difference is the more marked, the greater is the difference between the concentrations of sulphur in (1) and (2). The effect is particularly striking in experiments 12 to 15, where the differences in concentration of sulphur are greatest, and where, also, relatively large volumes of sol were taken for analysis.

An unequal distribution of chloride in the sense observed would arise if the volume occupied by the micelles in unit volume of the liquid was greater in

(1) than in (2), or if a Donnan equilibrium was established, in a manner similar to that previously described,[1] through the agency of the polythionate bound by the excess of sulphur in (1).

In order to assess the relative importance of the two factoss, it is necessary, in the first place, to ascertain the extent to which the colloidal micelles adsorb chloride under the given conditions. The amounts of adsorbed chloride, if any, must be deducted from the total amounts of chloride (found by analysis), in order to arrive at the concentrations of chloride in the intermicellar liquids - i.e., the concentrations which are of significance in the present connection. Moreover, the adsorption of chloride ions would augment the negative charge on the micelles and thus contribute to the Donnan effect. In actual fact, as the following considerations will show, adsorption of chloride is negligible under the experimental conditions employed in the present work.

---

(1) See "Introduction" pp. 4 - 6.

THE ADSORPTION of CHLORIDE by COLLOIDAL SULPHUR.

In Tables VII and VIII (pp. 33 and 34) are shown the actual experimental data obtained in the experiments in which sodium sols were coagulated by cooling, and the amounts of the various constituents in a given volume of liquid determined before and after coagulation. The concentrations of sulphur and chloride derived from the data in Table VII are recorded in Table XIII (a) (p. 49).

Let S_0 and $[Cl]_0$ be the respective concentrations of sulphur and chloride before coagulation, i.e., in the original sol, and S_s and $[Cl]_s$ be their concentrations after coagulation, i.e., in the supernatant liquid. Also, let V be the volume (in ml.) of the coagulum obtained from one litre of sol. Now Odén[1] has shown that coagulation is not accompanied by any appreciable change in the total volume of the system. Hence, assuming that chloride is <u>not</u> adsorbed by the colloidal sulphur, we have:

$$[Cl]_s = [Cl]_0 \cdot \frac{1000}{1000 - V} \qquad \text{(Equation 1)}$$

If the further assumption is made that the

---

(1) Odén, Nova Acta Upsala, Series IV, 3 (1913) No. 4, pp. 82 - 85.

TABLE XIII (b).

Polythionate.

Expt.	Concentration of polythionate (m.e./l.)			
	Bound		Free	
	Original sol	Supernatant liquid	Original sol	Supernatant liquid
1	64·42	25·83	-	-
2	48·27	26·56	9·69	10·74
3	74·84	22·76	27·94	31·16
4	90·01	58·12	22·84	25·91
5	103·0	11·47	24·22	27·61
6	-	-	-	-
7	93·89	18·41	15·34	16·31
8	105·4	13·56	13·16	16·31
9	106·2	9·12	16·95	19·62
10	98·65	18·48	12·59	15·50
11	110·5	31·16	39·40	44·24
12	66·43	3·07	19·13	20.99
13	123·9	64·25	16·55	17·76
14	121·4	52·79	16·63	17·93

coagulum consists of sulphur of density D, it follows that:

$$[Cl]_s = [Cl]_0 \cdot \frac{1000}{1000 - \frac{(S_0 - S_s)}{D}} \qquad \text{(Equation 2)}$$

or

$$D = \frac{[Cl]_s \cdot (S_0 - S_s)}{1000 \cdot ([Cl]_s - [Cl]_0)} \qquad \text{(Equation 3)}$$

It is generally accepted[1][2][3] that colloidal sulphur is in the amorphous condition. The "calculated" values of $[Cl]_s$ given in the last column of Table XIII (a) were obtained by means of Equation 2, on the assumption that the coagula consisted entirely of amorphous sulphur of density 1·90, the average of the values given in the International Critical Tables[4]. In every case the observed value of $[Cl]_s$ is <u>greater</u> than the calculated, by an amount which greatly exceeds the probable experimental error. This result means that if the coagulum consists of sulphur alone, the density of sulphur is considerably less than 1·90. Since this is highly improbable, it follows that the coagulum must contain water which is not acting as a solvent for the chloride; in other words the

---

(1) Odén, <u>loc. cit.</u>, p. 78.
(2) Freundlich and Scholz, Kolloid Chem. Beih., <u>16</u> (1922) 234.
(3) Bassett and Durrant, J.C.S., <u>1931</u>, 2919.
(4) Volume III (1928) p. 21. The value of 1·90 is in harmony with certain observations made in the course of the present work (see pp. 66, 67).

colloidal micelles are "hydrated".

For the purpose of discussion, however, it will be convenient to describe D as the "apparent density" of the sulphur, as calculated from the experimental data by equations of the same type as Equation 3. Values for D calculated from the observed values of $[Cl]_0$ and $[Cl]_s$, by means of Equation 3 itself, are shown in the first part of Table XIV (p. 53), and it will be seen that the mean value of D is 1·26, which is much less than 1·90.

The values of D obtained by the application of Equation 3 may be compared, in the first place, with those calculated by means of the similar equation:

$$D = \frac{[P_f]_s \cdot (S_0 - S_s)}{1000 \cdot ([P_f]_s - [P_f]_0)} \qquad \text{(Equation 4)}$$

where $[P_f]_0$ and $[P_f]_s$ are the respective concentrations of free polythionate before and after coagulation. The values of D so obtained are given in Table XIV. It should be noted that the concentrations of free polythionate employed in these calculations were determined by the barium sulphate method, and are therefore more accurate than the concentrations, for the same systems, given in Table XIII (b) (p. 50), which were determined by the silver sulphide method, as shown in Table VIII (p. 34).

It is evident that the values of D obtained with

TABLE XIV.

Coagulation by Sodium Chloride.

Table	Experiment	D.	S.H.V.
Reference substance: sodium chloride			
XIII (a)	1	1·28	1·49
"	2	1·52	1·25
"	3	1·11	1·71
"	4	1·07	1·78
"	5	1·32	1·44
"	6	1·48	1·28
"	7	1·21	1·57
"	8	1·17	1·62
"	9	1·22	1·56
"	10	1·17	1·62
"	11	1·35	1·41
"	12	1·24	1·53
"	13	1·16	1·64
"	14	1·23	1·55
X	3	1·41	1·35
"	4	1·17	1·62
	Mean	1·26	1·53
Reference substance: sodium polythionate.(1)			
XIII (b)	13	1·23	1·55
"	14	1·28	1·49
	Mean	1·26	1·52
Reference substance: sucrose.			
X	1	1·37	1·39
"	2	1·55	1·23
"	3	1·37	1·39
"	4	1·29	1·47
	Mean	1·40	1·37
Reference substance: raffinose.			
XI	3(2)	1·48	1·28
"	4(2)	1·43	1·33
"	5(3)	1·28	1·49
"	6(3)	1·30	1·46
	Mean	1·37	1·39

(1) Polythionate determined as sulphate. See Table II (i)(j)(k)(l).
(2) Lithium sol A.
(3) " " B.

Equation 4 closely agree with the corresponding individual values, and also the mean value of D, obtained with Equation 3. This agreement provides good evidence that there is little, if any, adsorption of chloride by the coagulum. The free polythionate is undoubtedly located in the intermicellar liquid, and since the relation between the concentrations of chloride before and after coagulation is obviously the same as that between the corresponding concentrations of free polythionate, it must be concluded that the whole of the chloride is also present in the intermicellar liquid.

This conclusion is supported by the coagulation experiments with sodium sols, in which sucrose or raffinose was used as reference substance. The appropriate experimental data are given in Tables X and XI (pp. 40 and 43). Employing the symbols shown in the tables, we have:-

$$D = \frac{(d).((a) - (b))}{1000 . ((d) - (c))} \qquad \text{(Equation 5)}$$

where (a) and (b) are the respective concentrations of sulphur before and after coagulation, and (d) and (c) are rotations directly proportional to the respective amounts of sugar in unit volume of liquid before and after coagulation. The values of D obtained are also given in Table XIV. They are definitely higher than

the average value obtained with chloride as reference substance, but the agreement is close enough to show that if the chloride is appreciably adsorbed, the sugars must be adsorbed to about the same extent. Since this is unlikely under the given conditions, it follows that the extent of the adsorption of any of the three substances may be regarded as negligible. It should be added that, as will be shown later, there are good grounds for supposing that the higher values of D obtained with the sugars may be due to dehydration by these substances. In experiments 3 and 4 from Table X, concentrations of chloride were determined before and after coagulation of a sol containing sucrose. The mean value of D is 1·29 when chloride, and 1·32 when sucrose, is taken as reference substance. Since, in this case, the degree of hydration must be the same for both reference substances, the agreement between these figures gives some support to the above view.

Odén[1] carried out a large number of experiments similar in type to those described above. In these experiments the temperature of the sol was lowered by stages. Sodium sols were investigated, and at each stage the concentrations of sulphur and sodium in the supernatant liquid were determined, the analytical procedure being as follows.[2] A known volume of the

---

(1) Odén, loc. cit., pp. 126 et seq.
(2) Odén, loc. cit., pp. 70, 71.

liquid was evaporated to dryness and the weight of the residue, consisting of sulphur and sodium salts, determined. The sulphur was then eliminated, by ignition, and the sodium estimated as sulphate. It was found, of course, that the progressive decrease in the sulphur content of the supernatant liquid was accompanied by a parallel decrease in the sodium content. Being unaware of the presence of sodium polythionate in his sols, Odén assumed that the sodium was present as chloride only. Hence he concluded from his experiments that chloride was strongly adsorbed by the sulphur micelles, and therefore carried down by the coagulum, when the sol was cooled.

It is evident that a very large part, if not all, of the sodium in the coagulum must have been in the form of polythionate. Actually, Odén's data are in agreement with this view, as the following considerations will show. Odén[1] found that in the case of a monodisperse sol, his results were expressed fairly closely by the relation:-

$$y = \frac{A\left(100 - \frac{S}{D}\right)}{100} + \beta S, \qquad \text{(Equation 6)}$$

where y = grams of "sodium chloride" and S = grams of sulphur in 100 ml. of sol (at any stage of the coagulation), A = grams of "sodium chloride" in 100 ml. of

---

(1) Odén, loc. cit., pp. 127, 128.

supernatant liquid after complete coagulation, β = grams of "sodium chloride" adsorbed by one gram of sulphur, and D = 2·0 (assumed density of colloidal sulphur). By rearrangement of the terms in Equation 6, we have:-

$$\beta = \frac{y - A}{S} + \frac{A}{100\ D} . \qquad \text{(Equation 7)}$$

In the following table are given mean values of β, calculated by means of Equation 7, but taking D = 1·3, the mean value found in the present work for the "apparent density" of the coagulated sulphur.

Table Oden[1]	Fraction of colloidal sulphur	A	y	S	β gram	β m.e.
41	0·08 - 0·10	0·59	-	-	0·0295	0·50
36	0·20 - 0·24	0·50	-	-	0·0417	0·71
37	"	0·94	-	-	0·0400	0·68
38	"	2·00	-	-	0·0426	0·73
39	"	2·06	-	-	0·0426	0·73
43	0·20 - 0·25	1·63	-	-	0·0477	0·82
40	0·30 - 0·35	2·06	-	-	0·0778	1·33
42*	Polydisperse	1·17	2·03	16·30	0·0537	0·92
			1·99	12·99	0·0640	1·10
			1·92	9·86	0·0770	1·32
			1·79	6·51	0·0961	1·64
			1·58	4·24	0·0976	1·67

On the assumption that there is no adsorption of chloride, the symbols in Equation 7 have the following significance: y = total concentration of sodium in sol,

(1) loc. cit., pp. 129-135.

* β is not a constant in this case.

A = concentration of sodium (as chloride and free polythionate) in intermicellar liquid, and β = amount of sodium corresponding to the polythionate bound by one gram of sulphur. Hence if the values of β obtained by Odén's method of calculation are divided by:

$$\frac{1000}{\text{molecular weight of sodium chloride}},$$

we obtain values, expressed in milliequivalents, for the polythionate bound by one gram of sulphur, provided there is no adsorption of chloride. The last column of the above table gives values of β obtained in this way. The values range from 0·51 to 1·67 m.e./g., and very similar values have been obtained by direct determination of the bound polythionate in undialysed sols, i.e., in sols of the same type as those investigated by Odén. Thus Bassett and Durrant's[1] values range from 0·40 to 1·19 and those of Bolam and Muir[2] from 0·34 to 1·13 m.e./g. In the present work (see Table XXII, p. 95), the values lie between 0·54 and 1·86 m.e./g. Hence, even if adsorption of chloride does occur, it can account for only part of the value of β.

Odén's results have been frequently quoted in the literature as representing the adsorption of

---

(1) Bassett and Durrant, loc. cit.
(2) Bolam and Muir, J.C.S., 1933, 1022.

chloride.[1][2][3][4] Freundlich[5] takes this view, even after his work with Scholz had revealed the presence of relatively large amounts of polythionate. Actually, Freundlich and Scholz's values for total polythionate range from 0·94 to 1·38 m.e./g., and are therefore comparable with the values of β in the last column of the above table. The misinterpretation is the more surprising in that Freundlich himself draws attention to the anomaly that, according to Odén's data, the amount of adsorbed chloride is independent of the concentration of chloride in the intermicellar liquid. This is illustrated by the values taken from Tables 36, 37, 38 and 39 of Odén's paper, which show that, for a given fraction of colloidal sulphur, β is practically constant, while A varies from 0·50 to 2·06. If β represents bound polythionate, however, there will be no question of variation with y, Thus the constancy of β supports the view that there is no adsorption of chloride.

The adsorption of chloride by colloidal sulphur has been studied by several workers, with apparently contradictory results. On the one hand, the results

---

(1) Gustaver, Kolloidchem. Beih., 15 (1922) 213.
(2) Svedberg, Colloid Symposium Monograph, 1 (1923) p. 18.
(3) Rinde, Phil. Mag. 7, 1 (1926) p. 35.
(4)Hatschek, Kolloid. Zeitschr., 11 (1912) 280.
(5) Freundlich, "Kapillarchemie", 4th ed., II (1932) p. 392.

of Rinde,[1] and those of Bolam and Bowden,[2] indicate that adsorption does take place. On the other hand, Bassett and Durrant,[3] and Bolam and Muir[4] found no evidence of adsorption in the sols they examined. It may be significant that the first set of workers investigated dialysed, and the other set (as in the case of Odén and also the present work), undialysed sols. At present it is not easy to suggest how the adsorption might be promoted by dialysis of the sol.

THE PROPERTIES of SULPHUR COAGULA.

In their classical paper on colloidal sulphur, Sobrero and Selmi[5] record certain observations on the properties of coagula produced by the addition of neutral salts to sols prepared by the interaction of sulphur dioxide and hydrogen sulphide in the presence of water. Sodium salts were found to produce coagula which redispersed to form the sol again if the supernatant liquid containing the sodium salt was decanted, and the coagulum then washed two or three times with water.

---

(1) Rinde, loc. cit.
(2) Bolam and Bowden, J.C.S., 1932, 2684.
(3) Bassett and Durrant, loc. cit., p. 2951.
(4) Bolam and Muir, loc. cit.
(5) See Hatschek, "The Foundations of Colloid Chemis try" (1929) p. 59; Odén, loc. cit., pp. 18 et seq.

In contrast with this, potassium salts gave "elastic" coagula which could not be repeptised even by repeated treatment with water. Later, Stingl and Morawski[1] reported that treatment with potassium or barium salts gave a "plastic modification" of sulphur, while calcium, magnesium or sodium produced the "ordinary flocculent form."

Similar observations were made by Odén[2] in the case of the coagula obtained from sols prepared by the interaction of sulphuric acid and sodium thiosulphate. Odén states that the sulphur is almost liquid when coagulated with hydrochloric acid, forms hard cakes with potassium salts, is pasty with barium salts, and is fine-grained, flocculent, etc. with copper sulphate and other salts. It was further found by Oden that in all cases, the coagulum is initially peptisable, but that with some coagulants, e.g., potassium and barium salts, the coagulum rapidly becomes non-peptisable. In the case of sodium salts, the coagulation is reversible, even after keeping the coagulum for an indefinite period.

Weiser and Cunningham[3] appear to be the first to study in any detail, or to attempt to explain, the influence of the nature of the coagulant upon the properties of the coagulated sulphur. Sols formed by

---

(1) Stingl and Morawski, J. prakt. Chem., (2) 20 (1879) 20.

(2) Odén, loc. cit., pp. 155, 157.

(3) Weiser and Cunningham, "Colloid Symposium Monograph", VI (1928) 319.

the interaction of sulphurous acid and hydrogen sulphide were investigated, and the coagulants employed were all chlorides. With hydrogen, lithium, sodium, iron, or aluminium as kation, the coagulation was found to be reversible; with copper, magnesium or zinc, "reversible on repeated washing"; with calcium, partly reversible; and with potassium, caesium, strontium or barium, irreversible. Portions of the coagula (described as "gelatinous") produced by lithium or sodium were treated with potassium, caesium or barium salts (which gave "plastic coagula") and their behaviour observed in the ultramicroscope. The clumps of aggregated particles were seen to shrink, and in some cases convection currents were observed, which were attributed to the release of water from the coagula. Weiser and Cunningham conclude that the coagula produced by lithium and sodium are "gelatinous" and "peptisable" because the colloidal particles are kept separated by layers of water due to the adsorption of the highly hydrated lithium and sodium ions. When treated with potassium, caesium or barium salts, the sodium or lithium ions are replaced by kations which are not sufficiently hydrated to maintain films of water capable of preventing coalescence of the colloidal particles to form "plastic" and non-peptisable aggregates.

Bassett and Durrant[1] found that in the case of

---

(1) Bassett and Durrant, loc. cit., p. 2930.

sols formed from sulphuric acid and sodium thiosulphate, the coagulum produced by potassium ions show little tendency to peptise. This is attributed to "secondary changes" which seem to occur in the coagulum after it is formed. Bassett and Durrant further state that "there are strong indications that these secondary changes are connected with the elimination of combined water from the coagulum, for they are much less marked with coagula produced by ions such as sodium, magnesium, nickel, cobalt, iron and copper, which have a strong tendency to remain hydrated, and these coagula readily redissolve in cold water; still more readily do those produced by lithium nitrate or by mineral acids". Thus Bassett and Durrant agree with Weiser and Cunningham in thinking that the behaviour of the coagulum depends upon the degree of hydration of the coagulating ion. However, no fresh evidence is adduced in support of this view.

In order to obtain more definite information with regard to the influence of the coagulating ion upon the behaviour of the coagulum, experiments were carried out, similar to those described in the previous section, but with lithium, potassium, barium salts and nitric acid (at 80°C.) as coagulants. The results are shown in Table XV (p. 64) which includes, for the sake of easy comparison, the mean values obtained with sodium chloride as coagulant (Table XIV). Sodium sols were

TABLE XV.

Table	Expt.	Coagulant	Reference Substance	D.	S.H.V.
Reversible Coagulation.					
XIV	Mean	Sodium chloride	Chloride	1·26	1·53
"	"	"	Polythionate	1·26	1·52
"	"	"	Sucrose	1·40	1·37
"	"	"	Raffinose	1·37	1·39
X	5	Lithium chloride	Sucrose	1·05	1·81
"	6	"	"	1·18	1·61
"	7	"	"	1·08	1·76
"	8	"	"	1·11	1·71
XI	1	"	Raffinose	1·39	1·37
"	2	"	"	1·41	1·35
Irreversible Coagulation.					
IX	4	Potassium nitrate	Chloride	2·38	0·80
"	5	"	"	1·74	1·09
X	9	Potassium chloride	Sucrose	1·89	1·01
"	10	"	"	1·82	1·04
"	11	"	"	2·00	0·95
"	12	"	"	1·90	1·00
IX	6	Barium nitrate	Chloride	1·74	1·09
"	7	"	"	1·88	1·01
X	13	Barium chloride	Sucrose	1·90	1·00
"	14	"	"	1·91	0·99
IX	1	Nitric acid	Chloride	1·95	0·97
"	2	"	"	1·94	0·98
"	3	"	"	1·89	1·01

used, except where raffinose was the reference substance, in which case lithium sols were employed. The table indicates where the actual experimental data for each experiment are to be found.

In addition to values of D, Table XV gives, in the last column, values of the "Specific hydrodynamic volume" (denoted by S.H.V., for convenience). As defined by Kraemer,(1) the specific hydrodynamic volume is the volume of coagulum (or of micelles) containing unit volume of sulphur. Thus, in terms of the symbols previously employed, and again assuming that the density of sulphur itself is 1·90, we have:

$$S.H.V. = \frac{V}{\frac{S_0 - S_s}{1{\cdot}90}} = \frac{1{\cdot}90}{D} \qquad \text{(Equation 8)}$$

In the case of each coagulant, it was ascertained by actual experiment whether the coagulum could be peptised by removing the supernatant liquid and treating the coagulum with water. At room temperature, the coagulua produced by sodium and lithium salts were readily peptised, but potassium and barium gave coagula which showed no tendency to redisperse. In the case of potassium, however, some peptisation occurred on heating to 80°C., provided the coagulum was fresh. It will be

---

(1) See Chapter XX, by Kraemer, in Taylor's "A Treatise of Physical Chemistry", II (1931) pp. 1615-1616.

seen that these results are in agreement with the observations by others.

The potassium and barium coagula were considered to be "granular" rather than "plastic", and the sodium and lithium coagula "flocculent" rather than "gelatinous". However, it is possible that these descriptions are not mutually exclusive.

Table XV shows that in the case of coagulation by sodium and lithium ions, i.e., reversible coagulation, the value of D is always considerably less than 1·90, whereas in the case of coagulation by potassium and barium, i.e., irreversible coagulation, the values of D are, with one exception, close to 1·90. The difference involved is perhaps brought out more strikingly by consideration of the values for the specific hydrodynamic volume. While S.H.V. is practically equal to unity in the case of potassium and barium, it is considerably higher than unity in the case of lithium and sodium. It must be concluded, therefore, that the potassium and barium coagula consist almost entirely of sulphur (of density 1·90), and that the lithium coagula, like those of sodium, are definitely hydrated, i.e., hold a considerable amount of water which does not function as a solvent for the reference substances employed. Hence these experiments provide direct evidence that the tendency of a coagulum to peptise depends upon the degree to which it is hydrated.

In the case of the coagula produced by treating the sols with nitric acid at 80°C., the mean value of D is 1·93, and that of S.H.V. is 0·99. Since the polythionate is known to be decomposed under these conditions (see p. 16), the question arises as to whether such decomposition also occurs in the case of coagulation by potassium and barium. To test this point, experiments were carried out as follows. On the one hand, the total polythionate in a portion of sodium sol was determined as silver sulphide by direct treatment with silver nitrate acidified with 0·2 N. nitric acid (which is insufficient to decompose the polythionate). On the other hand, the total polythionate was determined on a portion of sol coagulated by potassium nitrate and kept for some hours. The results obtained are shown below.

Expt.	Wt. of silver sulphide per 10 ml. of sol (gm.)	
	Uncoagulated sol	Coagulated sol
1	0·2146	0·2154
2	0·1791	0·1787

It is clear from these figures that the polythionate remains intact after coagulation with potassium salts. Bassett and Durrant[1] obtained similar results. They

(1) Bassett and Durrant, loc. cit., p. 2948.

observed, in addition, that the bound polythionate rapidly becomes free, due, presumably, to fusion of the sulphur particles, and the consequent reduction in the surface area.

THE HYDRATION of COLLOIDAL SULPHUR.

The first suggestion that a portion of the water in Odén sols is bound by the colloidal sulphur appears to have been made by Hatschek,[1] in order to account for Odén's[2] observation that the viscosity of the sols depends upon the degree of dispersion of the colloidal sulphur. According to Hatschek's interpretation, the sulphur particles are surrounded by layers of "adsorbed" water. On the basis of certain assumptions, Hatschek calculated from Odén's viscosity data[2] that in the case of an amicronic sol the volume occupied by the adsorbed layer amounts to about 62% of the volume occupied by the sulphur particle.

Some years later Freundlich and Scholz drew attention to the fact that Odén sols, in their general behaviour, resemble typical hydrophilic colloids, e.g., the proteins. In particular, the sulphur sols are relatively insensitive towards the coagulating action

---

(1) Hatschek, loc. cit.; see also Hatschek, "The Viscosity of Liquids" (1928) 199.
(2) Odén, loc. cit., pp. 85 et seq.

of acid and alkali metal salts, and the coagula produced by these substances are readily peptised. From the results of their own investigations, Freundlich and Scholz concluded that the hydrophilic behaviour of the colloidal sulphur is due to "hydration" through the agency of adsorbed polythionate. Freundlich and Scholz further suggested that attractive forces operate between the sulphur atoms of the polythionate and the sulphur particles, on the one hand, and between the oxygen atoms of the polythionate and the water molecules, on the other. According to Freundlich and Scholz, strong evidence of hydration is provided by the fact, that, for a given content of sulphur, Odén sols are very much more transparent than the typically hydrophobic Von Weimarn sols.

Dorfman[1] also interprets his intensive observations on the behaviour of Odén sols towards electrolytes and certain non-electrolytes, in terms of the charge and hydration of the micelles. Again, no direct evidence of hydration is advanced, and no explanation is given of the origin of the hydration.

As already shown, the results obtained in the present work have definitely established that the coagula produced by lithium and sodium salts are hydrated. It is therefore reasonable to suppose that the micelles in uncoagulated sols are also hydrated. This is fully

---

(1)Dorfman, Kolloid Zeitschr., 46 (1928) 186, 198 ; 52 (1930) 66. Dorfman and Ščerbačewa, Kolloid Zeitschr., 52 (1930) 289.

confirmed by determinations of the distribution of raffinose between two sols of unequal concentration, separated by a membrane permeable to substances in true solution, but impermeable to a portion of the colloidal sulphur. The actual experimental data are given in Table XII (p. 45). In these experiments, after equilibrium was established, equal volumes of the two sols were taken, the sulphur completely coagulated by the addition of barium salt, and the rotation produced by the sugar in the supernatant liquid determined. Under the given conditions, the supernatant liquid contains all the water, since barium coagula are not hydrated. Hence, if the micelles in the uncoagulated sol were not hydrated, the supernatant liquid would be simply the intermicellar liquid of the sol and, therefore, should have the same composition in the two cases. According to Table XII, however, the rotation produced by the supernatant liquid is always much higher in the case of the less concentrated sol (2) than in that of the more concentrated sol (1). This shows directly that the sulphur micelles in the sols themselves are hydrated. Coagulation by the barium salt releases the hydration water, which joins the supernatant liquid, and since the concentration of sulphur in (1) is greater than that in (2), the intermicellar liquid in (1) is diluted to a greater extent than that in (2). Hence the rotations produced by the supernatant liquids

differ in the sense observed.

Values of D and S.H.V. were calculated in the following manner. Let S_1 and S_2 be the concentrations (gm. per litre) of sulphur in (1) and (2) respectively, and let R_1 and R_2 be the respective rotations for the uncoagulated sols. Then:

$$R_1 = \text{Observed rotation for supernatant liquid from (1)} \times \frac{1000 - \frac{S}{1{\cdot}90}}{1000}$$

and

$$R_2 = \text{Observed rotation for supernatant liquid from (2)} \times \frac{1000 - \frac{S_2}{1{\cdot}90}}{1000}$$

the density of uncoagulated sulphur being taken as 1·90, since barium chloride was used as coagulant. Also

$$D = \frac{R_2(S_1 - S_2)}{1000(R_2 - R_1)} \qquad \text{(Equation 9).}$$

The results of the calculations are shown in Table XVI (p. 72), the values of R_1 and R_2 being shown in the second and the third columns.

The hydration data may now be considered as a whole. For this purpose, the mean values of the specific hydrodynamic volume are collected together in Table XVII (p. 72). In the first place, it will be seen that with sodium chloride as coagulant, the coagulum obtained from lithium sol B appears to be more hydrated than that from sol A. There is good reason to believe that the difference is real, since close agreement exists

TABLE XVI.

Distribution of raffinose in membrane equilibria.

Expt.	Rotation (degrees) calculated for		D.	S.H.V.
	(1)	(2)		
Sodium sol.				
1	29·67	31·66	1·07	1·78
2	26·61	30·68	0·89	2·14
3	40·28	43·21	0·96	1·98
Lithium sol.				
4	19·03	20·37	1·19	1·60
5	24·97	26·10	1·23	1·55

TABLE XVII.

Coagulant	Sol	Reference substance	Mean S.H.V.
Sodium chloride	Sodium	Chloride	1·53
"	"	Polythionate	1·52
"	"	Sucrose	1·37
"	Lithium A	Raffinose	1·31
"	Lithium B	"	1·48
Lithium chloride	Sodium	Sucrose	1·72
"	Lithium A	Raffinose	1·36
None	Sodium	"	1·97
"	Lithium	"	1·58

between the results of duplicate experiments (Table XIV). The experiments were performed with particular care. A 2-decimetre tube was employed to obtain relatively large values for the rotations, and the sols were completely coagulated, so that the supernatant liquid was completely clear, which favoured accurate measurement of the rotation. Since all four experiments were carried out on the same day, uncertainty due to temperature variation was eliminated. Finally, the sols were kept for a month before being used, which ruled out any significant disturbance due to ageing during the actual experiments.

Odén showed that the higher the degree of dispersion of the colloidal sulphur, the higher is the concentration of coagulant required to produce coagulation. This means that the particles in sol B were smaller than those in sol A. Since the specific hydrodynamic volume is greater in the case of B than in that of A, it seems safe to conclude from the present experiments that the finer is the state of subdivision of sulphur, the greater is the degree of hydration. Hence, since the specific surface area of colloidal particles increases with increase in degree of disperse, it appears highly probable that the hydration is confined to the surface of the micelle. With sodium chloride as coagulant and sucrose as reference substance, the mean value of S.H.V. is 1·37. In this case the sol

was not fractionated and it is therefore to be expected that the value of S.H.V. will fall between the value (1·31) obtained with lithium sol A and that (1·48) obtained with lithium sol M.

The values for coagulation with sodium chloride may now be compared with those obtained with lithium chloride as coagulant. With lithium sol A, and raffinose as reference substance, that is to say under identical conditions, S.H.V. for lithium (1·36) is somewhat higher than that for sodium (1·31). In the case of sodium sols, however, there is a much greater divergence, the value of 1·72 being obtained for lithium, and 1·37 for sodium. It is difficult to see how the state of the coagulum obtained with a given coagulating kation can depend upon the nature of the kation present in the original sol. Several workers[1][2][3] have shown that, under conditions similar to those of the present experiments, the counter-ions are completely replaced by those of the coagulating kations, so that the same coagulum is obtained with a given salt, irrespective of the nature of the original sol.

The results at least indicate that the hydration of lithium coagula is probably somewhat higher than that of sodium coagula. This may appear to conflict with the values of S.H.V. for uncoagulated sols. It

---

(1) Odén, loc. cit.
(2) Bassett and Durrant, loc. cit.
(3) Bolam etc., loc. cit.

would be anticipated that the hydration of the micelles with lithium as counter-ion, would not be less than that with sodium. Actually, S.H.V. for sodium was found to be 1·97, as compared with 1·58 for lithium. However, part, at least, of the discrepancy can be traced to the fact that the sulphur in the lithium sol was coarser than that in the sodium sol. The lithium sol was prepared by repeated coagulation with lithium chloride and it proved impossible to obtain a concentration of the salt large enough to coagulate the finer fractions of the sulphur.

The data in Table XVII further show that dehydration of the micelles occurs when the sulphur is coagulated, even with sodium chloride as coagulant.

COLLOIDAL SULPHUR and the DONNAN MEMBRANE EQUILIBRIUM.

The distribution of chloride in the membrane equilibrium experiments may now be considered in the light of the preceding discussion. Table XVIII (a) (p. 76) gives the concentrations of chloride and sulphur on the two sides of the membrane as calculated directly from the actual experimental figures contained in Table V (p. 30). It has been shown that adsorption of chloride by the colloidal sulphur is inappreciable and, therefore, that the whole of the chloride is present in

TABLE XVIII (a).

Distribution of sulphur and chloride in membrane equilibria.

Expt.	Concentration of sulphur (gm. per litre) (1)	(2)	Concentration of chloride (m.e./l.) (1)	(2)
		Sodium sols.		
1	-	-	64·55	67·84
2	-	-	41·15	44·75
3	-	-	33·39	36·13
4	43·59	6·39	25·65	28·00
5	12·35	-	47·62	48·63
6	30·28	3·34	70·36	73·65
7	23·37	3·37	22·36	24·13
8	9·07	1·14	14·25	14·63
9	24·52	4·08	28·26	30·00
10	26·28	12·17	8·29	8·99
11	35·33	3·764	35·60	37·84
12	77·66	18·87	26·33	29·95
13	102·5	12·04	24·59	29·32
14	80·81	18·45	26·79	30·28
15	63·25	22·42	25·50	27·76
16	47·48	24·16	22·70	23·76
		Hydrogen sols.		
17	27·86	1·40	25·43	27·17
18	24·18	2·58	188·5	190·4
19	27·85	0·20	54·79	57·81
20	13·16	0·10	4·18	4·78
21	42·00	0·24	10·15	11·94
22	7·90	0·06	2·89	3·18
23	8·92	2·46	2·29	2·69
24	17·70	7·97	2·69	3·18
25	17·28	5·62	1·79	2·19
26	6·40	1·88	1·29	1·49
27	13·86	2·52	3·08	3·48
28	28·49	5·50	3·06	3·95

TABLE XVIII (b).

Distribution of polythionate in membrane equilibria.

Expt.	Concentration of polythionate (m.e./l.)			
	Bound		Free	
	(1)	(2)	(1)	(2)
Sodium sols.				
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	32·37	5·65	-	-
5	16·55	5·41	3·47	4·68
6	28·90	4·12	1·13	0·89
7	18·32	2·02	0·65	1·53
8	9·61	3·79	3·47	2·83
9	21·88	5·17	-	-
10	30·99	14·86	4·12	5·33
11	38·26	7·43	4·12	4·68
12	82·56	20·66	10·49	13·08
13	81·53	14·36	-	-
14	78·14	22·76	-	-
15	66·12	27·12	-	-
16	52·47	30·84	-	-
Hydrogen sols.				
17	15·02	2·34	0·81	1·21
18	15·66	3·31	2·50	2·34
19	21·31	0·73	1·78	2·34
20	8·31	0·97	1·29	1·29
21	24·62	1·94	1·53	1·61
22	4·36	0·97	1·21	1·29
23	8·48	3·88	1·13	1·70
24	15·34	8·48	2·58	2·83
25	13·72	6·30	2·26	2·83
26	8·96	3·23	0·89	1·61
27	10·49	4·68	1·13	1·21
28	17·03	7·59	1·78	1·94

the intermicellar liquid of the sols. The problem now arises of deciding how far the unequal distribution of the chloride is due to the difference in the volumes occupied by the sulphur in (1) and (2).

Let $[Cl]_1$ and $[Cl]_2$ = the amounts (in milliequivalents) of chloride in 1 litre of sol (1) and of sol (2) respectively, $[Cl]_1'$ and $[Cl]_2'$ = the concentrations of chloride in the respective intermicellar liquids, S_1 and S_2 = the concentrations of sulphur, and D = the apparent density of the colloidal sulphur (assumed to have the same value throughout the system); then

$$[Cl]_1' = [Cl]_1 \cdot \frac{1000}{1000 - \frac{S_1}{D}} \qquad \text{(Equation 10)}$$

and

$$[Cl]_2' = [Cl]_2 \cdot \frac{1000}{1000 - \frac{S_2}{D}} \qquad \text{(Equation 11)}$$

The value obtained for the specific hydroxynamic volume of the micelles in sodium sols was 1·97 (see Table XVII). This value was determined in the presence of raffinose, and since the sugar may have some dehydrating action, the true value may be somewhat higher. For the purpose of the present calculations it will be assumed that S.H.V. is practically 2·0, and that D is practically 1·0.

In the following table are shown volumes of silver nitrate corresponding to the concentrations of chloride in the intermicellar liquid, as derived by Equations 10 and 11, in the case of experiments in which the difference between the experimental titres for (1) and (2) was particularly marked.

Expt.	Volume (ml.) silver nitrate required for 25 ml. intermicellar liquid		Difference.
	(1)	(2)	
10	6·11	6·53	0·42
11	18·92	19·47	0·55
12	20·49	21·92	1·43
13	19·66	21·30	0·64
14	20·39	21·60	1·21
15	19·05	19·87	0·82

The figures in the last column are quite outside the possible experimental error, and serve to show that after allowance is made, in the manner described, for the volume occupied by the micelles, there remains a significant difference between the concentrations of chloride on the two sides of the membrane.

If the unequal distribution of chloride entirely was/due to the difference between the volumes of sulphur in (1) and (2), conditions in the system would be represented by an equation of the same type as Equation 3, thus

TABLE XIX.

Expt.	$[Cl]_e$	S_1-S_e (= x)	$[Cl]_e-[Cl]_1$ (= y)	Ratio $\frac{y}{x}$
Sodium sols.				
6	75·65	26·94	3·29	0·12
11	37·84	31·57	2·24	0·07
14	30·28	62·36	3·49	0·06
9	30·00	20·44	1·74	0·09
12	29·95	58·79	3·62	0·06
13	29·32	90·46	4·73	0·05
4	28·00	37·20	2·35	0·06
15	27·76	40·83	2·26	0·06
7	24·13	20·00	1·77	0·09
16	23·76	23·32	1·06	0·05
8	14·63	7·93	0·38	0·05
10	8·99	14·11	0·70	0·05
Hydrogen sols.				
19	57·81	27·65	3·02	0·11
17	27·17	26·46	1·74	0·07
21	11·94	41·76	1·79	0·04
20	4·78	13·06	0·60	0·05
28	3·95	22·99	0·89	0·04
27	3·48	11·34	0·40	0·04
22	3·18	7·84	0·29	0·04
24	3·18	9·73	0·49	0·05
23	2·69	6·46	0·40	0·06
25	2·19	11·66	0·40	0·03
26	1·49	4·52	0·20	0·04

$$D = \frac{[Cl]_2.(S_1 - S_2)}{1000 . ([Cl]_2 - [Cl]_1)} \qquad \text{(Equation 12)}$$

from which we have

$$\frac{[Cl]_2 - [Cl]_1}{S_1 - S_2} = \text{constant}.[Cl]_2 \qquad \text{(Equation 13)}$$

Values for the ratio on the left-hand side of Equation 13 are given in Table XIX (p. 80), where the experiments are arranged in order of decreasing value of $[Cl]_2$. The figures show quite definitely that, while there may be some decrease in the value of the ratio (given under $\frac{y}{x}$) as the concentration of chloride falls off, the ratio does not vary in direct proportion to $[Cl]_2$. For example, taking the extreme cases only, while the value of $[Cl]_2$ in Experiment 6 is about eight times greater than in Experiment 10, and the value of $[Cl]_2$ in Experiment 19 is about thirty-nine times greater than in Experiment 26, in both cases the value of $\frac{y}{x}$ undergoes only a two- to threefold change. It is therefore evident that the whole of the unequal distribution of the chloride cannot be ascribed to the volume effect alone, but that some other effect must be present.

That the residual effect is a Donnan effect is strongly indicated by the experimental data. This is shown, in the first place, by comparison of the

TABLE XX.

Distribution of chloride and polythionate* in membrane equilibria.

(a)

Expt.	D = 1·0						
	$[Cl]'_1$	$[Cl]'_2$	$[P_f]'_1$	$[P_f]'_2$	$\frac{[Cl]'_2}{[Cl]'_1}$ (= W)	W^2	$\frac{[P_f]'_2}{[P_f]'_1}$ (=Z)
10	8·52	9·10	4·27	4·82	1·07	1·15	1·13
11	36·90	37·98	3·11	3·31	1·03	1·06	1·06
12	28·56	30·53	11·33	13·10	1·07	1·15	1·16
13	27·40	29·68	10·74	13·18	1·08	1·17	1·23

*Polythionate determined as barium sulphate. See Table II (e) (f) (m) (n) (g) (h) (o) (p).

(b)

Expt.	No Correction			D = 1·9			D = 0·5		
	W	W^2	Z	W	W^2	Z	W	W^2	Z
10	1·08	1·17	1·14	1·08	1·17	1·14	1·05	1·10	1·11
11	1·06	1·12	1·10	1·05	1·10	1·08	1·00	1·00	1·03
12	1·14	1·30	1·23	1·10	1·21	1·19	1·00	1·00	1·08
13	1·19	1·42	1·35	1·14	1·30	1·29	0·97	0·94	1·10

distribution of the chloride with that of the free polythionate. Let $[P_f]_1$ and $[P_f]_2$ be the amounts (milliequivalents) of free polythionate in 1 litre of intermicellar liquid in (1) and (2) respectively. Then since the polythionate ion is bivalent and the chloride ion univalent, the following relation will hold if the ions are distributed according to the theory of Donnan.(1)

$$\frac{[P_f]'_1}{[P_f]'_2} = \frac{([Cl]'_1)^2}{([Cl]'_2)^2} \qquad \text{(Equation 14)}$$

In Table XX (p. 82) are given values for the intermicellar concentrations of the free polythionate, calculated from equations of the same type as Equations 10 and 11, thus

$$[P_f]'_1 = [P_f]_1 \cdot \frac{1000}{1000 - \frac{S_1}{D}} \qquad \text{(Equation 15)}$$

and

$$[P_f]'_2 = [P_f]_2 \cdot \frac{1000}{1000 - \frac{S_2}{D}} \qquad \text{(Equation 16)}$$

the value of D being taken as 1·0. The values of

---

(1) Donnan, Z. Elektrochem., 17 (1911) 572.
Donnan and Garner, J.C.S., 115 (1919) 1314.

$[P_f]_1$ and $[P_f]_2$, i.e., the amounts of free polythionate in 1 litre of sol, are given in Table II (p. 21). They were determined by the barium sulphate method, and are therefore more accurate than those determined by the silver sulphide method (Table XVIII (b)). The figures in the last three columns of part (a) of Table XX show that the value (Z) of the ratio of the intermicellar free polythionate concentrations is much nearer to that (W^2) of the square of the ratio of the corresponding chloride concentrations than to that (W) of the simple ratio itself. Thus, the Donnan relation (Equation 14) is fulfilled.*

Part (b) of Table XX shows how W, W^2, and Z are affected by the particular assumption made with regard to the volume occupied by the micelles. It will be seen that if no correction is made for this volume, or if the micelles are assumed to be unhydrated (D = 1·90), Z is uniformly less than W^2, while if the hydration is taken as large enough to make D = 0·5, Z is uniformly greater than W^2. This result indicates that the hydration must be such as to give D a value lying between 0·5 and 1·9, in harmony with the values obtained from the raffinose experiments. Actually, with D = 1·0, Z is in two cases higher, and in two cases lower than

---

* It may be noted that in the coagulation experiments, $[P_f]_o/[P_f]_s = [Cl]_o/[Cl]_s$. Hence no Donnan effect is present in the system: coagulum — supernatant liquid.

W^2. Thus the true value of D is probably not far removed from 1·0, but more accurate data are required to fix its value by means of membrane equilibrium experiments.

If the whole of the unequal distribution of chloride were due to the Donnan effect, the following relation would hold[1]

$$[P] = \frac{[Cl]_2^2 - [Cl]_1^2}{[Cl]_1} \qquad \text{(Equation 17)}$$

where [P] = concentration of that part of the bound polythionate in (1) responsible for the Donnan effect. The right-hand side of the above equation may be expressed as

$$2([Cl]_2 - [Cl]_1) + \frac{([Cl]_2 - [Cl]_1)^2}{[Cl]_1} ,$$

the second term of which becomes negligible compared with the first term when $[Cl]_1$ is large compared with [P]. Under these conditions, since [P] is approximately proportional to $S_1 - S_2$, it follows that

$$\frac{[Cl]_2 - [Cl]_1}{S_1 - S_2} = \text{Constant} \qquad \text{(Equation 18)}$$

i.e., the ratio of differences would be independent of $[Cl]_2$. It was previously shown that if the whole of

---

(1) See "Introduction", p. 5.

unequal distribution were due to the volume effect, the ratio of differences would be directly proportional to $[Cl]_2$. Now the experimental figures given in the last column of Table XIX, though only approximate, indicate that the value of the ratio, while not independent of $[Cl]_2$, decreases less rapidly than $[Cl]_2$. Hence the experimental values support the view that, actually, the Donnan effect and the volume effect are both present.

The assumption has been made throughout that the concentration of non-diffusible sulphur = $S_1 - S_2$. It may be pointed out here that the true concentration will be somewhat greater than this difference. Since part of the volume in (1) is occupied by non-diffusible sulphur, the concentration of diffusible sulphur will be less than S_2, so that something less than S_2 should be deducted from S_1. However, the error involved by taking $S_1 - S_2$ is without significance in the present connection. Similar considerations, of course, apply to the difference $S_0 - S_3$ in the case of coagulation experiments.

THE CONSTITUTION of ODÉN SOLS.

The primary object of investigating the distribution of the chloride in the membrane equilibria was to determine the proportion of counter-ions "adhering" to the micelle. If it be assumed for the moment that the

TABLE XXI.

Expt.	Bound polythionate (m.e./l.) By analysis $[P]_a$	By Donnan theory Uncorrected $[P]$	By Donnan theory Corrected $[P]'$	$\frac{[P]}{[P]_a}$	$\frac{[P]'}{[P]'_a}$
		Sodium Sol			
1	-	6·76	-	-	-
2	-	7·52	-	-	-
3	-	5·71	-	-	-
4	26·72	4·92	2·79	0·18	0·10
5	11·14	2·04	-	0·18	-
6	24·78	6·73	2·68	0·27	0·11
7	16·30	3·67	2·69	0·23	0·17
8	5·82	0·78	0·55	0·13	0·09
9	16·71	3·59	2·36	0·21	0·14
10	16·13	1·46	1·20	0·09	0·07
11	30·83	4·64	2·19	0·15	0·07
12	61·90	7·73	4·08	0·12	0·07
13	67·17	10·37	4·76	0·15	0·07
14	55·38	7·43	3·49	0·13	0·06
15	39·00	4·72	2·39	0·12	0·06
16	21·63	2·16	1·03	0·10	0·05
		Hydrogen Sol			
17	12·68	3·60	2·15	0·28	0·17
18	12·35	3·80	-	0·31	-
19	20·58	6·20	2·95	0·30	0·14
20	7·34	1·29	1·15	0·18	0·16
21	22·68	3·90	2·88	0·17	0·13
22	3·39	0·61	0·56	0·18	0·17
23	4·60	0·87	0·82	0·19	0·18
24	6·86	1·07	1·00	0·16	0·15
25	7·42	0·89	0·84	0·12	0·11
26	5·73	0·43	0·41	0·08	0·07
27	5·81	0·85	0·76	0·15	0·13
28	9·44	2·04	1·86	0·22	0·20

volume occupied by the sulphur is inappreciable, then, according to the arguments previously advanced (p. 6), the proportion of non-adhering counter-ions is given by the ratio $[P] / [P]_a$. $[P]$ is defined by Equation 17, and $[P]_a$ is the concentration of polythionate bound by the excess of sulphur in (1) ; in other words, the difference between the total concentration of bound polythionate in (1) and (2), as found by analysis. Values of the above ratio are given in Table XXI (p. 87), where $[P]_a$ is the difference between corresponding figures in the second and third columns in Table XVIII (b) (p. 50)*. It will be seen that only a small proportion of the bound polythionate is exerting any Donnan effect. That is to say, even if no allowance is made for the volume effect, the results indicate that the bulk of the counter-ions are adhering to the micelles.

In the last column of Table XXI are given the values of the ratio when the necessary correction for the volume of the sulphur is applied, i.e., when all concentrations are referred to the intermicellar liquid. Thus,

$$[P]' = \frac{([Cl]'_2)^2 - ([Cl]'_1)^2}{[Cl]'_1} \qquad \text{(Equation 19)}$$

---

* The actual experimental data are shown in Table VI (p. 31).

$$\text{and } [P]'_a = [P]_a \times \frac{1000}{1000 - \frac{S_1 - S_2}{1{\cdot}0}} \quad \text{(Equation 20)}$$

In view of the given experimental conditions, no stress can be laid on the individual values of the ratio, but the figures do indicate that only about 9% of the bound polythionate is operative in the case of sodium sols, and about 15% in the case of hydrogen sols.

It should be noted that in calculating [P] and $[P]'$, any effect of the free polythionate, always present in the intermicellar liquid of the sols, was disregarded. Strictly speaking, the concentrations of the sodium ions corresponding to the free polythionate ions should be included in the values of $[Na^+]_1$, and $[Na^+]_2$ in the Donnan equation of ionic products (see pp. 5 and 6). However, the only appreciable effect of making allowance for the free polythionate would be to increase the values of [P] and $[P]'$ in the case of the more dilute hydrolgen sols, where the concentrations of free polythionate are more or less comparable with those of chloride.

It was further assumed (pp. 5 and 6) that the product of the activity coefficients of the sodium and chloride ions was the same for (1) and (2). Now, since the ratio of the free polythionate concentrations is equal to the square of the ratio of the chloride concentrations (see p. 84), it follows that the

activity of the chloride ion must be the same for (1) and (2). Hence, the fundamental assumption really made is that a proportion of the sodium ions in a sulphur sol is without activity, while the remainder has the same activity as in a solution of sodium chloride of the same concentration with respect to chloride as the intermicellar liquid. It would be more exact to regard the activity of the sodium ions as varying continuously with their distance from the surface of the micelle, i.e., from the negative charges of the bound polythionate anions. In any case, however, it is evident that a very large proportion of the sodium counter-ions have a very low activity. Hence it is reasonable to conclude that, actually, the bulk of these ions have lost their activity because they "adhere" to the micelle, or, in other words, are so closely associated with the bound polythionate anions that their individuality with respect to charge and osmotic behaviour has disappeared.

This conclusion is in harmony with the results of certain investigations by other workers. Bjerrum[1] studied the osmotic pressure and membrane potentials in the case of colloidal chromic hydroxide. From his osmotic data he concluded that about 90% of the chlorine counter-ions are "associated" with or "adsorbed" on the chromic hydroxide micelles (positively charged,

---

(1) Bjerrum, Zeitschr. physikal Chem., 110 (1924)p.676.

probably by adsorbed chromium or hydrogen ions). Rinde[1] has calculated from Bjerrum's values for membrane potentials that the true figure is somewhat lower, namely, about 75%. In any case, only a small proportion of the counter-ions are considered to be detached from the micelles.

Ghosh[2] investigated the membrane equilibrium in the case of sols prepared by the peptisation of stannic oxide by sodium hydroxide. The ratio of distribution of the total sodium on the two sides of the membrane was found by analysis to be 8·7, whereas the ratio of the sodium ions calculated from the membrane potential was only 1·94. Hence, Ghosh states that "the greater proportion of the colloidal complex containing NaO is undissociated, and only a small portion dissociates into a colloidal anion and the Na^+ kation." Since the sol is stabilised by adsorbed stannate, this means that only a small proportion of the corresponding sodium counter-ions are in the "undissociated" condition.

McBain and Thomas[3] have carried out determinations of the transference numbers of the iron and chlorine in a ferric hydroxide sol, stabilised by adsorbed ferric or hydrogen ions. Both the moving

---

(1) Rinde, Phil. Mag. (7) 1 (1926) p. 49
(2) Ghosh, J.C.S., 1929, 2290.
(3) McBain and Thomas, J. Physical Chem., 40 (1936)997.

boundary and Hittorf methods were employed, and the results showed close agreement. The interesting and, from the present point of view, significant observation was made that 89·5% of the chlorine counter-ions travelled to the cathode. Thus the bulk of the counter-ions were carried in the positive colloidal particles. McBain and Thomas describe the ions so carried as being in the "un-ionised" or "undissociated" unconducting form".

Investigation of the electrical conductivity, transference numbers, and osmotic behaviour of long paraffin-chain salts has revealed that the constitution of their solutions varies in a characteristic manner with the concentration of the salt. In sufficiently dilute solution the salt is present in the form of simple positive and negative ions and behaves as a normal strong electrolyte. With increase in concentration, however, the paraffin-chain ions aggregate into colloidal micelles. At the same time, the activity coefficient of the oppositely-charged ions (alkali metals, halides, etc.) decreases to a marked extent, and a proportion of these ions travel with the micelles when a current is passed through the solution. Thus the state of affairs is very similar to that existing in sulphur and hydroxide sols. In the case of paraffin-chain salt solutions, G. S. Hartley[1] pictures

(1) Hartley, "Aqueous Solutions of Paraffin-Chain Salts" (1936) p. 32 ; Trans. Faraday Soc., 34 (1938) 1284; Kolloid Zeitschr., 88 (1939) 22.

the simple inorganic counter-ions which are ineffective in regard to charge and osmotic behaviour, as "adhering" to the micelles. By "adherence" Hartley does not appear to imply more than what the word usually signifies, and it has been thought advantageous to borrow the term for the case of colloidal sulphur. To describe the counter-ions as being"adsorbed" on the micelles, or as being"associated", or as forming "unionised molecules", with the bound polythionate, may suggest an unwarranted degree of knowledge of the forces involved.

Rinde[1] measured the osmotic pressure of hydrogen sulphur sols dialysed until free of chloride. The membrane potentials and the activities of the hydrogen ions inside and outside the membrane were also determined. From the electrometric data the concentrations of the non-adhering hydrogen counter-ions were calculated by means of Donnan's equation. According to Rinde's data, the observed osmotic pressure is several times less than that expected. Rinde suggests that this may be due to the so-called"Hammarsten"effect, but in view of the results of the present experiments, it seems probable that the e.m.f. data are in error. For example, in the case of the sol of fraction 0·3 - 0·4, there are, according to Rinde, 0·52 milliequivalents of bound polythionate per gm. of sulphur to which

---

(1) Rinde, loc. cit.

hydrogen ions are not adhering. Now, Odén obtained the figure of 1·33 milliequivalents for (β) the total bound polythionate per gm. of sulphur of fraction 0·3 - 0·35 (see p. 57). Hence (see p. 89), there will be 1·33 × 9/100 = 0·11 milliequivalents to which counter-ions are not adhering. Thus Rinde's value may be as much as five times too high and this would largely account for the fact that his calculated value for the osmotic pressure of the sol concerned is about seven times greater than the observed value.

In view of Rinde's results it was decided, in the case of the present investigation, to employ direct analytical methods as being probably more reliable than electrometric methods. The use of analytical methods made necessary the preparation of relatively large quantities of colloidal sulphur, but it was felt that the time and labour involved were justified under the circumstances.

In Table XXII (p. 95) are shown the amounts of polythionate bound by one gm. of sulphur in most of the sols investigated. The values are similar to those obtained by other workers (see p. 58). It will be seen that the values for "supernatant liquid" are greater than those for "original sol", and also that the values for "sol (2)" are greater than those for "sol (1)". The conclusion is that the amount of bound polythionate per unit mass of sulphur increases as the size of the

TABLE XXII.

	Expt.	Polythionate (m.e.) per gram sulphur.	
		Original sol	Supernatant liquid
	1	0·76	1·08
	2	0·73	1·20
	3	1·07	1·45
	4	0·90	1·00
	5	0·90	1·70
Coagulation	6	-	-
experiments	7	0·97	1·44
Data Table XIII.	8	1·02	1·67
	9	1·07	1·76
	10	1·02	1·37
	11	0·97	1·63
	12	0·94	1·28
	13	1·00	1·58
	14	1·02	1·74
	Mean	0·95	

		(1)	(2)
	4	0·74	(0·88)
	5	1·34	-
	6	0·95	1·23
	7	0·78	(0·60)
Membrane	8	1·06	(3·33)
equilibrium	9	0·89	1·27
experiments	10	1·18	1·22
Data Table XVIII	11	1·08	1·97
Sodium Sol	12	1·06	1·10
	13	0·80	1·19
	14	0·97	1·23
	15	1·05	1·21
	16	1·11	1·28
	Mean	1·00	

TABLE XXII. (cont.).

	Expt.	Polythionate (m.e.) per gram sulphur	
		(1)	(2)
Hydrogen sol	17	0·54	1·67
	18	0·65	1·28
	19	0·77	(3·65)
	20	0·63	(9·70)
	21	0·59	(8·08)
	22	0·55	(16·20)
	23	0·95	1·58
	24	0·87	1·06
	25	0·79	1·12
	26	(1·40)	1·72
	27	0·76	1·86
	28	0·60	1·38
	Mean	0·70	

particle decreases. This is in harmony with the results of Odén, already quoted (p. 57), and provides evidence that the polythionate is adsorbed on the surface of the particles.

Another feature of the data in Table XXII is that the value of the ratio: concentration of bound polythionate/concentration of sulphur is definitely less, in the case of hydrogen sols, than in the case of sodium sols. The reason for this difference is not obvious.

In the case of the sodium sols, which were very reproducible, the bound polythionate amounted to about 1·0 milliequivalent per gm. sulphur. If the specific hydrodynamic volume of the micelles is 2·0 (see p. 78), and the density of the sulphur is 1·90, there will be 1·0 gram of non-solvent water (density taken as 1·0) to 1·90 grams of sulphur, or 1/18 × 1·9 = 30 millimols of water to 1 gram of sulphur, i.e., to one milliequivalent of bound polythionate. If the non-solvent water arises from the hydration (using this term in its widest sense) of the polythionate and the adhering sodium ions, the amount of such hydration is therefore 60 mols water per mol polythionate ($Na_2S_xO_6$), or 20 mols water per gram-ion of polythionate or sodium, assuming equal distribution between the three ions. In view of the wide range of ionic hydration values to be found in the literature,[1] it may be said that the above figure is, at the least, not unreasonable.

---

(1) Glasstone, "The Electrochemistry of Solutions", 2nd ed., (1937) Chapter III.

THE COAGULATION Of COLLOIDAL SULPHUR.

The value of 15% was provisionally assigned to the proportion of non-adhering counter-ions in hydrogen sols, on the assumption that D = 1·0 (the value obtained experimentally for sodium sols). In any case, the proportion cannot be greater than 17%, the value derived on the assumption that the micelles in hydrogen sols are not hydrated (D = 1·9). Hence the proportion of adhering hydrogen ions is not less than 83%, as compared with 91% in the case of sodium ions. The magnitude of these values, and the small difference between them, make it improbable that adherence of the counter-ions (that is to say, their mere attachment to the bound polythionate) is sufficient to account for the coagulating action of the electrolytes, as suggested by Bolam and co-workers, on the basis of their data for ionic interchange in sulphur sols. A survey of the relevant literature shows that the coagulation value of hydrochloric acid is always several times that of sodium chloride. It appears unlikely that the concentrations required to bring about 100% adherence would differ to anything like this extent. The conclusion is that coagulation involves some other type of union, of a more intimate nature than adherence, between the counter-ions and

the polythionate ions.

A similar state of affairs exists in the case of long paraffin-chain salts. McBain, Willavoys and Heighington[1] maintain that the large increase in viscosity which results from the addition of sodium chloride to a solution of sodium palmitate is due to the linking up of the "neutral" micelles to form "ramifying aggregates". However, the above workers consider that the concentration of sodium chloride required is far in excess of that necessary to simply convert the "ionic" micelles to "neutral" micelles, i.e., in Hartley's terminology, to cause the sodium ions to adhere to the paraffin-chain micelles. McBain and his co-workers therefore conclude that the mere formation of neutral micelles is not, in itself, sufficient to produce aggregation, but that the concentration of the salt must be such as to dehydrate the neutral micelles.

The present investigation has shown that in the case of colloidal sulphur dehydration does actually occur, and to an extent depending upon the nature of the coagulating kation. On the view that coagulation is due to dehydration of the counter-ions and of the bound polythionate ions, the coagulating power of a salt will depend, other things being equal, upon the ease with which the kation is dehydrated. Thus the

---

(1) McBain, Willavoys and Heighington, J.C.S., 1927, 2689.

more strongly hydrated the kation, the lower will be its coagulating power. Hence in the case of alkali metal salts, the order of decreasing coagulating power will be the order of increasing hydration, and this is the sequence found experimentally.

It will have been noted (p. 63) that Bassett and Durrant appear to regard the dehydration as due to "secondary changes" occurring after coagulation. This is rather surprising, since these workers consider that coagulation results from the formation of an insoluble complex polythionate, and hence must surely involve dehydration of the ions concerned.

Since lowering the temperature will decrease the dehydration of the ions in the micelles (as may be deduced from its effect on the solubility of simple salts), the tendency of the sols to coagulate will become more marked, the lower is the temperature, as happens in actual practice.

The coagulating action of sucrose is very interesting and does not appear to have been previously noted. In view of the high oxygen content of the sugar molecule, it may be expected to strongly attract water and hence to dehydrate the ions present in the sol. As has been already pointed out (p. 55), the present data indicate that some dehydration does occur.

It is clear that the tendency of the kation of a given salt to interchange with the counter-ion of a

hydrogen sulphur sol does not depend upon the ease with which it adheres to the bound polythionate, as suggested by Bolam and co-workers. In view of the results of the present investigation, it must be assumed that the replacing power of an added kation is determined by the readiness with which it enters into the more intimate type of union involving dehydration. This hypothesis is obviously more satisfactory than the other, in that it provides a more reasonable explanation of the fact that in the case of the alkali metal kations the order of increasing replacing power is also the order of decreasing hydration.

Kruyt and Verwey[1] maintain that the ionic interchange is not an essential feature of the coagulating process. It is evident, however, that in the case of Odén sulphur sols, interchange must occur for coagulation to take place whenever the coagulating kations are not of the same nature as the counter-ions of the original sol.

---

(1) Verwey and Kruyt, Chem. Reviews, 16 (1935) 407 ; "Symposium on the Dynamics of Hydrophobic Suspensions and Emulsions" (1937), reprinted from Chem. Weekblad, 35 (1928) 77.

SUMMARY.

1. The micelles in sulphur sols of the Odén type have been investigated by determinations of the distribution of sulphur, chloride, polythionate and raffinose in membrane equilibria.

2. The coagula from Odén sols have been investigated by determinations of the distribution of sulphur, chloride, polythionate, sucrose, and raffinose between coagulum and supernatant liquid.

3. It has been found that:

i. under the given conditions, adsorption of chloride by the colloidal sulphur is inappreciable. Odén's data for the so-called "adsorption of sodium chloride" apply to the adsorption of polythionate.

ii. the micelles are hydrated, in the sense that non-solvent water is associated with the sulphur.

iii. the hydration per unit mass of sulphur increases with decrease in particle size.

iv. coagulation with lithium or sodium salts is accompanied by partial dehydration of the micelles.

v. practically complete dehydration occurs when the sols are coagulated by potassium or

barium salts.

vi. the colloidal sulphur gives rise to the Donnan type of distribution of electrolytes across a membrane.

vii. the observed Donnan effect accounts for only a small proportion of the polythionate ions bound by the micelles.

viii. the sols may be coagulated by the addition of sucrose, which has a dehydrating action upon the micelles.

ix. the density of the colloidal sulphur shows it to be non-crystalline.

x. the polythionate in Odén sols is completely oxidised when heated at 100°C. with 0·5 N. nitric acid.

xi. an equivalent amount of silver sulphide is obtained when the polythionate is heated with slight excess of silver nitrate in the presence of 0·20 N. nitric acid. The yield of silver sulphide is too high in the presence of 0·16 N. nitric acid.

4. It is concluded that in Odén sols:

i. the bulk of the counter-ions adhere to the bound polythionate ions.

ii. adherence of the counter-ions is insufficient to account for coagulation by electrolytes.

iii. coagulation by electrolytes results from some type of union between the kations of the coagulant and the bound polythionate ions, involving dehydration of the micelles.

iv. other things being equal, the coagulating power of the added kation and its tendency to undergo ionic interchange depends upon the ease with which it is dehydrated.

v. the tendency of the coagulum to peptise depends upon the extent to which the micelles have been dehydrated.

In conclusion, the author wishes to express his sincere thanks to Dr T. R. Bolam for his encouragement and guidance throughout the course of this investigation.